FACTORS CONTROLLING THE RESISTANCE OF OHMIC CONTACTS TO GERMANIUM TELLURIDE

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by

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ABSTRACT

Ohmic contacts with extremely low resistance and controlled morphologies are required to improve the performance of GeTe-based radio frequency (RF) switches. These contacts also require good thermal stability, since GeTe is a phase change material that switches back and forth between the amorphous and crystalline states through controlled Joule or laser heating. In this thesis, the role of metal selection, pre-metallization surface treatments, and post-metallization annealing on the resistance of Ohmic contacts to GeTe is examined.

X-ray photoelectron spectroscopy (XPS) was used to characterize surfaces of polycrystalline α-GeTe films after different surface treatments, including UV-O₃, \textit{in-situ} Ar⁺ ion etching, deionized water (DI H₂O), ammonium sulfide (NH₄)₂S, and hydrochloric acid (HCl), in an effort to understand the effect of pre-metallization surface treatments on the resistance of different metal/GeTe contacts. The combination of UV-O₃ and subsequent oxide removal procedures affect the GeTe surface stoichiometry, as does Ar⁺ plasma without UV-O₃ treatment. Ar⁺ plasma, DI H₂O, and (NH₄)₂S preparations leave the GeTe surface richer in Ge compared to the HCl treatment, which leaves the surface Te-rich.

The thesis focuses on contacts based on three different metals: Ni, Au, and Mo. The trend in the as-deposited specific contact resistance ($\rho_c$) as a function of surface treatments demonstrated a strong dependence on the choice of the metal used. For Ni-based contacts, different surface treatments resulted in $\rho_c \approx 4 \times 10^{-8}$ Ω.cm², except for the HCl treatment, which resulted in contacts with much higher resistance, due to formation of a 5nm thick layer of Ni₁.₂⁹Te at the interface. A constant $\rho_c \approx 1.2 \times 10^{-8}$ Ω.cm² was found for Au (100 nm) contacts, regardless of the surface treatment used. For Mo-based contacts, \textit{in-situ} Ar⁺ plasma treatment provided the lowest $\rho_c \approx 7 \pm 1 \times 10^{-9}$ Ω.cm². These measurements were made using a refined transfer length method (RTLM) test structure; we found that our circular transfer length test structure (CTLM) provided inaccurate results due to the effect of the metal sheet resistance on the extraction of such very low values of specific contact resistance.
We discuss how phase diagrams can be used to understand interfacial reactions and predict which metallizations could provide long-term thermal stability. As expected from our calculated phase diagram, Auger electron spectroscopy (AES) and cross-sectional transmission electron microscopy (TEM) revealed that reaction occurs between Ni and GeTe, even at room temperature. After annealing, there is an increase in contact resistance along with serious morphological changes in the metallization. Au contacts are unreactive on GeTe, even after annealing at 350 °C for 30 min. However, volatilization of tellurium still occurs through openings that appear in the gold film. Mo-based contacts may be reactive, but the kinetics of the reaction are much slower than the Ni case. An increase in \( \rho_c \) values was observed after annealing, regardless of the metallization.

The similarity of as-deposited contact resistances obtained with very different metal work functions points to Fermi level pinning at the surface of GeTe. Moreover, the low values of the specific contact resistances correspond to low Schottky barrier heights. Finally, this thesis points to possible routes to maintain the lowest achievable \( \rho_c \) without loss of thermal stability.
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DEDICATION

This thesis is dedicated to my mother.
Chapter 1
Background

1.1 Introduction

Chalcogenide-based phase change materials (PCMs) are of great interest due to their contrasting electrical behaviors upon crystallization and amorphization\(^1\). PCMs exhibit different physical properties such as electrical resistivity and optical reflectivity when switched back and forth between the crystalline and amorphous phases, giving these materials the ability to store information\(^2\). PCMs usually contain one element of group VI, and PCMs containing Ge, Sb and Te are the most common, with Ge\(_2\)Sb\(_2\)Te\(_5\) (GST) being the most studied material to date. PCMs have been implemented in a variety of applications such as non-volatile random access memories (RAM)\(^{3,4,5,6}\), rewritable compact discs (CDs) and digital video discs (DVDs)\(^{7,8,9,10,11,12}\), and radio frequency (RF) switches\(^{13,14,15,16,17,18}\).

In PCM-based RF switches, the state of the switch is controlled by the set (ON) and reset (OFF) processes corresponding to the “amorphous to crystalline” and “crystalline to amorphous” transitions, respectively\(^{16}\). The transition between the ON and OFF states is accomplished by heating via Joule heater made of NiCrSi\(^{14}\). A short electric pulse as short as 30 ns\(^{19}\) with high amplitude is used to raise the GeTe temperature above its melting temperature (~ 725 °C\(^{20}\)) followed by fast quenching of the melt to switch the device off. The fast quenching is needed to lower the probability of atom rearrangements in the structure, resulting in the amorphous state. To change the state of the switch, a longer electric pulse with moderate amplitude is applied to raise the temperature slightly above the crystallization temperature, allowing atoms to arrange themselves, resulting in the low resistance crystalline phase. Figure 1.1 illustrates the switching principle in PCM-based RF switches.
1.2 The Phase Change Material GeTe

1.2.1 Properties of GeTe

Polycrystalline germanium telluride (c-GeTe) is an intrinsic p-type, degenerate semiconductor with narrow optical bandgap of 0.73-0.95 eV, corresponding to high hole concentrations of \((10^{20}-10^{21} \text{ cm}^{-3})\). GeTe exhibits metallic conductivity due to the large concentration of Ge vacancies in the material. The Fermi-level \((E_F)\) often reported to be below the valence band edge by \(~0.3-0.5\) eV, corresponding to the high hole concentration \((10^{20} \text{ to } 10^{21} \text{ cm}^{-3})\). More recently, attempts to n-type dope the GeTe with donors such as Bi and Pb have been conducted.

Amorphous GeTe films can be prepared via sputtering, evaporation, and atomic layer deposition (ALD) of GeTe sources and precursors. GeTe nanowires were also grown using a metal catalyst-mediated vapor-liquid-solid process. The amorphous GeTe films are then crystallized either by furnace annealing or laser annealing above the crystallization temperature of GeTe \((\sim 190-230 \, ^\circ\text{C})\). Crystallization of GeTe films can be induced also by heating the substrate while depositing. The annealing temperature has a great influence on the film properties, as well as, the substrate material. Good
adhesion between the GeTe film and the substrate required. A substrate that can accommodate the increase in the GeTe volume with annealing is very important. Different substrates were used such as SiO$_2$, Si$_3$N$_4$, Al$_2$O$_3$, mica, and Corning glass. For example, films deposited on Corning glass peeled off when heated above 300 °C. On the other hand, heating the Corning glass at 100 °C while depositing resulted in pushing the delamination temperature of GeTe to 400 °C.

At room temperature, GeTe crystallizes in the rhombohedral crystal structure (α-GeTe) (space group: R3m), as shown in Figure 1.2, which can be viewed as a distorted NaCl-type structure. The deviation from the NaCl structure is seen in the angle $\alpha=88.35^\circ\neq90^\circ$ and the atomic parameter $x=0.237\neq0.25$, which describes the relative displacement of the Ge and Te sublattices of GeTe along the [111] direction. It is important to mention that GeTe has another stable yet hard-to-form Te-rich phase termed as γ-GeTe that has an orthorhombic crystal structure (space group: Pnma). At 430 °C, the α-GeTe undergoes a displacive phase transition from rhombohedral (space group: R3m) to the high temperature phase β-GeTe that has the cubic crystal structure (space group: Fm3m). Amorphous GeTe crystallizes to α-GeTe in a short time (~10 ns) and at a recrystallization temperature of about 190 °C, which is relatively high compared to GST (150 °C). Crystalline α-GeTe exhibits hole mobility in the range of 15-120 cm$^2$/Vs.

![Figure 1.2: Crystal structure of α-GeTe at room temperature.](image-url)
1.2.2 GeTe–based RF Switches

High performance RF switches required for reconfigurable electronics must exhibit an extremely low insertion loss, high OFF/ON ratio, fast switching times, low power consumption, and excellent reliability\(^1^6\). PCM-based switches exhibit zero power consumption in the steady-state operation, making them non-volatile devices compared to metal oxide semiconductor (MOS) and micro-electro-mechanical systems (MEMS) systems switches\(^1^3\), and making incorporation of PCMs as the active switching material in RF switches very appealing. GeTe switches are viable candidates and have been reported for RF applications\(^1^3,1^4,1^5,1^6,1^7,1^8,3^6,3^7\). Among all of the PCMs, germanium telluride (GeTe) has one of the lowest ON-state resistivities\(^2^1\) of about 1.6x10\(^{-4}\) \(\Omega\) cm. Non-volatile GeTe switches were reported to demonstrate an ON-state insertion loss of 0.1–0.24 dB and high dynamic range (OFF/ON ratio) of about 2\(\times\)10\(^7\) times\(^1^4,1^6,1^8\).

However, parasitic resistances from the Ohmic contacts can be a limiting factor in the performance of PCM-based RF switches. The contact contributes to a non-negligible fraction of the ON-state resistance of the switch\(^3^8\). One solution to this problem is the optimization of Ohmic contacts with extremely low resistances and well-controlled morphologies, allowing for extremely high-performance operation of PCM-based RF switches.

1.2.3 Need for Low Contact Resistances to GeTe

To illustrate the need for low contact resistance in RF switches, it is instructive to look at the cutoff frequency (\(F_{co}\)) that represents the maximum frequency of unity gain and is the figure of merit of RF switches. The switch cutoff frequency, defined as\(^1^3\)

\[
F_{co} = \frac{1}{\pi R_{ON} C_{OFF}} \quad (1.1)
\]

where \(R_{ON}\) is ON-state resistance and \(C_{OFF}\) is the OFF-state capacitance. The ON-state resistance can be divided into three different resistance contributions\(^3^9\), defined as

\[
R_{ON} = 2R_c + 2R_{electrode} + R_{PCM} \quad (1.2)
\]
where $R_c$ is the contact resistance, $R_{\text{electrode}}$ is the metal electrode resistance and $R_{\text{PCM}}$ is the resistance due to incomplete crystallization of the phase change material\textsuperscript{39}. Choosing low resistivity metals for metallization such as Au can reduce $R_{\text{electrode}}$. It is evident that the reduction of the contact resistance is essential to reduce the ON-state resistance in order to meet the requirements of high-frequency RF applications. Furthermore, with the aggressive scaling of devices to smaller dimensions, the contact resistance becomes a serious hurdle that limits further progress. Therefore, high-quality Ohmic contacts are required to reduce the parasitic resistance of the RF switch and improve its frequency response.

1.3 Metal/Semiconductor Contacts

When a metal is brought into contact with semiconductor, a potential barrier ($\phi_B$) forms at the interface, which controls the current transport through the contact\textsuperscript{40}. Engineering the barrier height and width is one of the most important concepts of Ohmic contact engineering. The barrier can alter the current transport mechanisms producing either an Ohmic contact or rectifying contact. In order to establish Ohmic contact, a low barrier height or/and width is important in order to maximize the current conduction through thermionic emission and tunneling mechanisms, respectively.

1.3.1 Schottky-Mott Model

When a p-type semiconductor is contacted by a metal with a lower work function, the Fermi levels ($E_{\text{Fs}}$ and $E_{\text{Fm}}$, respectively) must line up to reduce the energy of the system and establish thermal equilibrium. Holes from the semiconductor flow to the metal forming a depletion region with a characteristic width ($w_d$) in the semiconductor. The bands bend and a potential barrier ($\phi_B$) is formed at the interface as shown in Figure 1.3a. In the figure, the terms $E_{\text{vac}}$, $E_v$, and $E_c$ represent the vacuum level, the valence band, and conduction band levels, respectively. The figure illustrates the simplest case of a metal/semiconductor contact as described by the Schottky-Mott model\textsuperscript{40}, where the barrier height to holes is described by the metal work function ($\phi_m$) and the semiconductor bandgap ($E_g$) and electron affinity ($\chi_s$) as follows\textsuperscript{40};
\[ \phi_b = (E_g + \chi_s) - \phi_m \quad (1.3) \]

Here, \( \phi_b \) has a direct correlation to the metal work function. Considering equation (1.3), one can establish a zero barrier height by choosing a metal with high work function as in Figure 1.3b. This model is not always true experimentally.

![Diagram](image)

**Figure 1.3**: Schematic of band profiles before and after a metal and a degenerate p-type semiconductor are brought into contact when (a) \( \phi_m > \phi_s \) and (b) \( \phi_m < \phi_s \).

**1.3.2 Bardeen Model and Fermi Level Pinning**

In practical metal/semiconductor contacts, the barrier height may be independent of the metal work function due to Fermi level pinning resulting from surface/interface states, as proposed by Bardeen\(^{40,41}\). The termination of the semiconductor surface is not the same as in the bulk. Formation of dangling bonds that result in surface reconstruction might
induce defect and surface states. Additionally, sometimes the semiconductor surface is exposed to air prior to metallization, resulting in formation of oxides on the semiconductor surface, which alter the interface. The interaction between the metal and semiconductor at the interface also might alter the interface by introducing defects or reacted phases resulting in different properties than the bulk. Another theory behind the origin of the surface/interface states and Fermi level pinning is the metal-induced gap states (MIGS) theory.\(^{42}\) The exponential decay of the electron wave function of the metal into the semiconductor result in formation of states inside the bandgap of the semiconductor that tend to pin the Fermi level in the bandgap.\(^{42}\) Regardless of their origin, surface/interface states play an important role in determining the final \(\phi_b\) by pinning the Fermi level at the charge neutrality level \((\phi_{\text{CNL}})\). The latter describes the continuous distribution of the surface states at the metal/semiconductor interface.\(^{40}\) The barrier height is then independent of the metal work function and given by \(^{40}\)

\[
\phi_b = E_g - \phi_{\text{CNL}} \quad (1.4)
\]

Kurtin et al.\(^{43}\) have defined a pinning parameter \((S)\), with a value from 0 to 1 (corresponding to complete Fermi level pinning and no pinning, respectively) to describe the relationship between the barrier heights and the metal work function based on testing various metals with a wide range of electronegativity on the same semiconductor. Ionic semiconductors tend to show a strong dependence between the barrier height and the metal work function \((S \rightarrow 1)\). On the other hand, covalently bonded semiconductors result in weak dependence between the barrier height and the metal work function and correspond to \(S = 0\). The strong pinning at the interface between metal and covalently bonded semiconductors can be attributed to the high density of surface/interface states in covalently bonded semiconductors.

### 1.3.3 Current Transport Mechanisms

Current transport mechanism at the metal/semiconductor interface is influenced by the barrier height.\(^{42}\) In a p-type semiconductor, holes are the majority carriers and responsible for current transport across the metal/semiconductor interface. Current
transport happens through three principal mechanisms (Figure 1.4): thermionic emission (TE), thermionic field emission (TFE), and field emission (FE) based on the barrier height and width\textsuperscript{41} at the metal/semiconductor interface. TE current transport usually happens for semiconductors with low doping concentrations and large depletion widths (w\textsubscript{d}). The holes are thermally excited over the barrier. Field emission is common for heavily doped semiconductors wherein the narrow depletion width allows holes to tunnel through the barrier\textsuperscript{41}. TFE is the intermediate case that involves both thermal excitation and tunneling.

\begin{figure}
\centering
\includegraphics[width=0.5\linewidth]{fig1_4}
\caption{Schematic of energy band diagram showing TE, TFE, and FE transport across the Schottky barrier in a metal/p-type semiconductor interface.}
\end{figure}

\textbf{1.3.4 Characterization of Metal/Semiconductor Interfaces}

The specific contact resistance (\(\rho_{c}\)) measured in (\(\Omega\cdot\text{cm}^2\)) is an intensive property that is considered as the typical figure of merit of Ohmic contacts. \(\rho_{c}\) allows systemic comparison of different metallizations, defined as \textsuperscript{44}

\[\rho_{c} = \left(\frac{\partial V}{\partial J}\right)_{V=0} \quad (1.5)\]

where \(V\) is the applied voltage and \(J\) is the current density across the metal/semiconductor interface. The expression for the current density depends on the predominant current transport mechanism. Hence, \(\rho_{c}\) is commonly expressed as a function of the predominant current transport mechanism\textsuperscript{41}.
Thermionic emission (TE):

\[ \rho_c = \frac{k}{qA^*T} \exp \left( \frac{q\phi_b}{kT} \right) \] (1.6)

Thermionic field emission (TFE):

\[ \rho_c = \frac{k^2 \cosh \left( \frac{E_{00}}{kT} \right)}{qA^* \pi \left( q\phi_b + q\xi \right) E_{00}^{1/2}} \left[ \coth \left( \frac{E_{00}}{kT} \right) \right]^{1/2} \exp \left[ \frac{q(\phi_b - \xi)}{E_{00} \coth \left( \frac{E_{00}}{kT} \right)} + \frac{q\xi}{kT} \right] \] (1.7)

Field emission (FE):

\[ \rho_c = \frac{A^*\pi q}{k \sin \left( \pi C_1 kT \right)} \exp \left( \frac{-q\phi_b}{E_{00}} \right) - \frac{A^* q}{C_1 k^2} \exp \left( \frac{-q\phi_b + C_1 q\xi}{E_{00}} \right)^{-1} \] (1.8)

where \( C_1 = \left( 2E_{00} \right)^{-1} \ln \left[ \frac{4(\phi_b - V)}{\xi} \right] \) (1.9)

where \( E_{00} \) is the the characteristic tunneling energy, defined as

\[ E_{00} = \frac{\hbar q}{4\pi} \sqrt{\frac{N_A}{m^* \varepsilon_s}} \] (1.10)

where \( T \) is the temperature (in K), \( k \) is Boltzmann constant \((8.62 \times 10^{-5} \text{ eV})\), \( N_A \) is the acceptors impurities density \((\text{in cm}^{-3})\), \( m^* \) is the hole effective mass, \( \hbar \) is Planck constant \((4.13 \times 10^{-15} \text{ eV.s})\), \( \varepsilon_s \) the permittivity of the semiconductor, and \( q \) is the electron charge \((1.6 \times 10^{-19} \text{ C})\). \( \xi \) is the difference between the valence band and the Fermi level and negative for degenerate semiconductor, and \( A^* \) is the Richardson constant \((120 \text{ m}/\text{m}_e \text{ cm}^2/\text{K}^2)\).

It is evident that specific contact resistance is a function of \( \phi_b \) for all current transport mechanisms. Additionally, TE shows a great dependence on the temperature, whereas FE exhibits limited dependence on temperature.
1.4 Ohmic Contacts to GeTe

1.4.1 Introduction

In order to fabricate Ohmic contacts to GeTe, a metal or compound with a large work function might be best, at least based on the Schottky-Mott model. Quantitatively speaking, a metal with a work function larger than or equal to the summation of GeTe electron affinity ($\chi_{\text{GeTe}} = 3.8$ eV) and band gap ($E_g = 0.72$ eV) is required ($\phi_m = 4.52$ eV). Many metals satisfy this condition. However, GeTe is a covalently bonded semiconductor, and according to Kurtin et al., a pinning parameter ($S$) close to 0 is expected.

Another route to form Ohmic contact to GeTe is to heavily dope the GeTe. However, GeTe is already a degenerate semiconductor with a high hole concentration due to Ge vacancies, so it is not clear if further doing is possible or would be benficial.

1.4.2 Review of Ohmic Contacts to GeTe

Few authors have described Ohmic contacts to p-GeTe. Chua et al. have used high-resolution x-ray photoelectron spectroscopy (HRXPS) to estimate the band alignment parameters by characterizing GeTe/SiO$_2$ interface and deducing the c-GeTe band offsets relative to the band edges of the SiO$_2$. Band alignment parameters of c-GeTe are listed in Table 1.1. Afterwards, the hole barrier heights at Ni/c-GeTe, W/c-GeTe, and Al/c-GeTe interfaces were deduced using HRXPS. Zero barrier heights (negative) were found for Ni, W, and Al, which means that there is no barrier at the interface to prevent hole injection from the semiconductor into the metal, and vice versa. Chua et al. have reported a near complete Fermi level pinning in metal/c-GeTe interfaces.
Table 1.1: Band alignment parameters of c-GeTe from reference (39).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (in eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Work function ($\phi$)</td>
<td>4.9 ± 0.2</td>
</tr>
<tr>
<td>Band gap ($E_g$)</td>
<td>0.72</td>
</tr>
<tr>
<td>Electron affinity ($\chi$)</td>
<td>3.8 ± 0.2</td>
</tr>
<tr>
<td>Fermi level ($E_f$)</td>
<td>0.4 (below the top of the valence band)</td>
</tr>
<tr>
<td>Pinning parameter (S)</td>
<td>0.016</td>
</tr>
<tr>
<td>Charge neutrality level ($\phi_{CNL}$)</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Additionally, the contact resistances of Ni, W, and Al, in addition to Ti$_{30}$W$_{70}$ (TiW), to GeTe were studied. Chua et al.$^{39}$ used 50 nm Ni, W, and TiW followed by 150 nm Al as the metal contact to c-GeTe. The lowest specific contact resistance ($\rho_c$) of $8.6\times10^{-9}$ $\Omega$.cm$^2$ was achieved for the as-deposited Ni/Al (50/100 nm) contacts to c-GeTe using the circular transfer length method (CTLM) test structure. In this work, we will show that CTLM test structures are not the best way to accurately measure the contact resistivity due to the contribution of the metal sheet resistance. Specific contact resistances and hole barrier heights reported in Chua et al.$^{39,38}$ as a function of the metal contact are summarized in Table 1.2. A higher contact resistance was found for Al contacts to GeTe, even in the absence of a hole barrier. Even though the barrier height of W and Al were the same, however, the trend in the contact resistance was different, indicating that the barrier height is not the only parameter controlling the contact resistance.
Table 1.2: Summary of specific contact resistance and holes barrier height of different metals reported by Chua from Carnegie Mellon University\(^\text{39}\).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Specific contact resistance (Ω.cm(^2))</th>
<th>Barrier height (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>8.6 × 10(^{-9})</td>
<td>-0.2 ± 0.2</td>
</tr>
<tr>
<td>W</td>
<td>1.40 × 10(^{-8})</td>
<td>-0.1 ± 0.2</td>
</tr>
<tr>
<td>Al</td>
<td>1.40 × 10(^{-7})*</td>
<td>-0.1 ± 0.2</td>
</tr>
<tr>
<td>TiW</td>
<td>1.43 × 10(^{-8})</td>
<td>-</td>
</tr>
</tbody>
</table>

* The value is extracted from Figure 4.7(a) in reference (39).

Although Chua et al.\(^\text{38}\) studied the effect of annealing on amorphous a-GeTe contacts and the evolution of the a-GeTe resistivity upon crystallization, no studies of annealed contacts were performed on c-GeTe. Additionally, Chua et al. have highlighted the importance of pre-metallization surface treatments and low base pressure of the vacuum system during deposition and reported a reduction in the specific contact resistance using \textit{in-situ} Ar\(^+\) plasma cleaning and depositing at lower base pressure.\(^\text{39}\)

Chua et al.\(^\text{39}\) have reported that thermionic emission is the predominant transport mechanism on metal/GeTe. However, in the absence of a barrier to holes at the metal/GeTe, the current conduction cannot be described by the thermionic emission model, which involves exciting holes over the barrier. The mechanism of current transport across the metal/c-GeTe is not well established.

El-Hinnawy et al.\(^\text{14}\) used Ti/Pt/Au as a contact to their low-loss RF switches; however, no contact resistance measurements were reported\(^\text{14}\). Moreover, the same group used 1 µm of Ti/Au metallization on 75 nm of GeTe\(^\text{15}\). Contact resistance of 9.85 × 10\(^{-3}\) Ω.mm was achieved; however, no test structures details were presented.

Thermally stable contact to GeTe is crucial for PCMs based devices, just as low contact resistance is. Since the contacts will be subjected to heat treatment during device
processing and packaging, as well as modest heating during switching. To avoid reaction when the contact is heated, a contact in thermodynamic equilibrium with GeTe could be chosen. On the other hand, reactions might lower the contact resistance if we control them. Therefore, the thermodynamics of the metal-Ge-Te systems is important to gain insight about the stability of the contact at room temperature and elevated temperatures. Loubriat et al. have proposed that a thin Ti adhesion layer is necessary between the GeTe and the electrodes for mechanically and thermally stable contacts. They have studied the thermal stability of Ti/GeTe (20/100 nm) contacts by annealing the samples at two different temperatures (250 and 400 °C) for 15 min in argon. Characterized by both grazing incidence X-ray powder diffraction (GIXRD) and time of flight secondary ion mass spectrometry (TOF-SIMS), no evidence for chemical interaction occurs between Ti and GeTe at 250 °C. Annealing at 400 °C yielded formation of a Ti$_3$Te$_4$ intermetallic phase and segregation of elemental Ge.

We therefore conclude that when designing Ohmic contacts for GeTe, the selection of the metal and optimized surface preparations, deposition methods, and interfacial reactions are critical factors of study.
Chapter 2
Experimental Methods

2.1 Sample Fabrication

2.1.1 Samples Definitions and Test Structure Geometries

Polycrystalline p-type α-GeTe with a high hole concentration of (~$10^{20}$ cm$^{-3}$) and 110 nm thickness was sputtered on a Si substrate with a 100 nm thick amorphous Si$_3$N$_4$ barrier layer for this study$^{15}$. A schematic of the GeTe films used in this study is shown in Figure 2.1. The sheet resistance of GeTe films varies slightly from wafer to wafer. The average sheet resistance extracted from the four-point probe method performed on multiple wafers was $40 \pm 4 \Omega.\square^{-1}$.

![Figure 2.1: Schematic illustration of a cross section of GeTe wafers used in this thesis.](image)

For electrical measurements, both circular transfer length method (CTLM) and “refined” transfer length method (RTLM) test structures were patterned with nominal gap spacings of 0.6–20 µm. For the as-deposited samples all gap spacings from 0.6 to 20 µm are used. For annealing studies only gaps ≤ 2 µm are used due to the significant impact of annealing on the GeTe between the contact for gaps > 2 µm, which will be explained in details in section 2.7.2.1. Scanning electron microscopy (SEM) micrographs of CTLM and RTLM structures are shown in Figure 2.2a and 2.2b, respectively. The reason behind using these two different test structures will be discussed in a later section.
2.1.2 Samples Fabrication via Photolithography

1 x 1 cm samples were degreased in acetone, isopropanol, and deionized water for 5 min each with ultrasonication for 10 s each and then blown dry with compressed nitrogen. Standard contact photolithography procedures were used to pattern CTLM and RTLM test structures. The CTLM test structures involve one photolithography stage to define the structure, whereas the RTLM involves a second stage to isolate the mesas. Various photolithography procedures were tested first for a compatible photolithography process on GeTe. Initial patterning revealed the vulnerability of GeTe to tetramethylammonium hydroxide-based (TMAH) developers such as CD-26. The exposure of GeTe surface to CD-26 resulted in etching of the GeTe layer with time. This was undesirable and would introduce some uncertainty about the GeTe layer thickness and uniformity. Hence, a second process involving using poly(methyl methacrylate) (PMMA) as a protecting layer for GeTe was developed and standardized.

Prior to lithography, samples were heated to 115°C for 5 min to remove any water vapor on their surfaces. CTLM and RTLM test structures were fabricated by spin-coating the samples with a bi-layer of the PMMA A6 950/SPR3012 resist stack. Then samples were exposed in a GCA 8000 i-Line Stepper for 0.39 s. Then, samples were developed in CD-26 for 55 s. CD-26 development stops at the intermixed layer created between PMMA and SPR3012, which cannot be removed except by ashing in O₂ plasma. Then, the samples
were flooded in deep UV flood exposure for 30 min and developed in toluene. The detailed description of the 1st stage of photolithography used is below:

1. Dehydration-bake on hot plate at 115 °C for 3 min and cool for 1 min.
2. Spin-coat with PMMA A6 950 at 2.5 krpm for 45 s (400 nm thick).
3. Bake on hot plate at 180 °C for 3 min and cool for 2 min.
4. Spin-coat sample with SPR 3012 at 4.5 krpm for 45 s and bake on hot plate at 95 °C for 60 s (1.2 µm thick). (Dispensing of the SPR 3012 resist should be fast to have a uniform intermixed layer and thereby a uniform O₂ plasma etching rate.)
5. Expose for 0.39s using the GCA 8000 i-line Stepper.
7. Inspect using optical microscope.
8. Use O₂ plasma to ash the intermixed layer formed between PMMA and 3012 (O₂ flow of 250sccm, He flow of 50 sccm, power of 450 Watt, base pressure < 40 mtorr, and working pressure of 600 mtorr for 8:35 min).
9. Flood with DUV for 30 min.
10. Develop in toluene for 20s, rinse with DI H₂O, and dry with N₂. (This time may vary based on the thickness of PMMA left after the O₂ plasma step.)
11. Inspect using optical microscope.

Note that the O₂ plasma ashing is performed in the MetroLine IPC M4L plasma cleaner using the conditions listed in the process above.

2.2 Surface Preparation Procedures and Vacuum Pumpdown

The contact resistance dependence on different surface preparation procedures was investigated in this work. Those surface preparation procedures can be classified into two different categories: wet etchants and in-situ Ar⁺ plasma treatment. Surface preparation procedures used in the work are summarized in table 2.1.
2.2.1 Wet Etchants

After patterning, the samples were treated inside a PR-100 UV-Ozone Photoreactor (UVP Inc., San Gabriel, CA) for 10 min at 1 SLPM. Samples were placed 4 cm below the lamp to remove organic contaminants and to grow a uniform oxide layer. Afterwards, the oxide was etched with different oxides removal treatments, namely, ammonium sulfide (\((NH_4)_2S\)), hydrochloric acid (HCl) and deionized (DI) water. For \((NH_4)_2S\)-treated samples, the concentration of (100:1) DI H$_2$O:22–24\%(NH$_4$)S$_2$ was used for 30 s. For HCl-treated samples, a (10:1) DI H$_2$O:37\%HCl solution was used for 120 s. After each treatment the sample was rinsed with DI water for 15 s and blown dry with N$_2$. If instead only DI water was used as a surface treatment, the sample was treated for 5 min. Note that different concentrations were initially tested at the beginning to ensure that those chemicals would not attack and completely etch the semiconductor. For example, using a very highly concentrated (10:1) H$_2$O:(NH$_4$)$_2$S solution would etch the semiconductor in a few seconds.

2.2.2 Ar$^+$ Plasma

An in-situ Ar$^+$ plasma was used in the deposition chamber with Ar flow rate of 10 sccm and power of 375 Watt at a pressure of 3×10$^{-4}$ torr for 120 s. Also, no UV-O$_3$ treatment was used prior to this treatment.

Table 2.1: Summary of surface preparation procedures used in the contact resistance study in this work.

<table>
<thead>
<tr>
<th>Preparation Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 120 s Ar$^+$ plasma</td>
</tr>
<tr>
<td>2 10 min UV-O$_3$ treatment, 5 min water, 15 s water rinse N$_2$ dry.</td>
</tr>
<tr>
<td>3 10 min UV-O$_3$ treatment, H$_2$O:HCl (10:1) 2 min, 15 s water rinse, N$_2$ dry.</td>
</tr>
<tr>
<td>4 10 min UV-O$_3$ treatment, H$_2$O:(NH$_4$)$_2$S (100:1) 30 s, 15 s water rinse, N$_2$ dry.</td>
</tr>
</tbody>
</table>
2.3 Electron Beam Deposition, Metal Selection and Metal Stacks

2.3.1 Electron Beam Deposition

Wet etchant treated samples were loaded in Kurt J. Lesker AXXIS e-beam evaporation system with base pressure $< 2\times10^{-7}$ torr. Before deposition, a Ti getter was performed to lower the pressure $< 1\times10^{-7}$ torr by reducing the oxygen content in the chamber. While samples were shielded from the electron beam source, 30nm of Ti was deposited for gettering.

On the other hand, the metal depositions of the Ar$^+$ plasma-treated samples were carried out in the Kurt J. Lesker Lab-18 e-beam evaporation system with base pressure $< 2.5\times10^{-7}$ torr. No Ti getter was performed prior to metallization of the Ar$^+$ plasma samples. Samples were subjected to cooling at $5\ ^\circ\ C$ after depositing at least 5 nm of the metal contact due to the short distance between sources and the sample. Without cooling the sample, liftoff problems were encountered due to the excessive heat from the sources.

For all samples, cool-down periods are introduced between each metal deposition and the following metal deposition to minimize sample heating. A 15 min cool-down period is introduced between each deposition except for Pt where a 30 min cool-down period is introduced after each 7.5 nm deposition of Pt.

2.3.2 Choice of Contact Metallization

The choice of metallization is one of the contributing factors in determining Ohmic contacts to GeTe.

2.3.2.1 Nickel Based Contacts

Ni contacts have been explored and a low contact resistance ($R_c$) of $5.3\times10^{-3}$ $\Omega$.mm was achieved\textsuperscript{38}. These contacts consisted of sputtered Ni/Al (50 nm/ 150 nm) and used Ar$^+$ plasma as the pre-metallization surface treatment. However, circular transfer length method (CTLM) was used to extract this contact resistance, which can underestimate $R_c$. In section 2.6.3, we will show how the test structure used in the literature to evaluate the contact to Ni-based contacts was not the most accurate way to do so. In addition, the use of sputtering needs more complex fabrication procedures due to increased difficulty of
liftoff. Moreover, the evolution of the Ni based contacts to crystalline GeTe as a function of annealing has not been fully explored. Chua et al.\textsuperscript{38} studied the effect of annealing on the amorphous GeTe but not the crystalline GeTe. Therefore, we wanted to start with a metal that has been studied as a baseline for our processing.

2.3.2.2 Gold Contacts

Au has high work function (5.1 eV)\textsuperscript{47} comparable to Ni; hence, is expected to produce a lower barrier height on GeTe based on the Schottky-Mott model. Also, Au is in thermodynamic equilibrium with GeTe and no reaction is anticipated\textsuperscript{48}. Moreover, the elemental contact is easier to fabricate from the thermodynamic point of view compared to the alloyed contact. However, one should keep in mind that the Au-Ge system has a low eutectic temperature of 361 °C\textsuperscript{49}.

2.3.2.3 Molybdenum Based Contacts

Molybdenum has a relatively lower work function (4.6 eV)\textsuperscript{47} than Ni and Au; however, it has a high melting point which might enhance the contact stability.

2.3.3 Metal Stacks

A summary of metal thicknesses used in this thesis is listed in Table 2.2. The metals were used have the following purities: Ni (99.99%), Au (99.999%), Pt (99.99%), Ti (99.995%), and Mo (99.9%).
Table 2.2: A summary of metal thicknesses used in this work.

<table>
<thead>
<tr>
<th>Contact</th>
<th>Thicknesses (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Ti/Pt/Au</td>
<td>30/15/15/100</td>
</tr>
<tr>
<td>Au</td>
<td>100</td>
</tr>
<tr>
<td>Mo/Ti/Pt/Au</td>
<td>5/15/15/100</td>
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<td>15/15/15/100</td>
</tr>
<tr>
<td>Mo/Au</td>
<td>35/100</td>
</tr>
</tbody>
</table>

2.4 Metal Contact Liftoff and Mesa Fabrication

Liftoff is performed in positive radiation resist edge bead remover (EBR PG from MicroChem), which contain 70–80% 1,3-dioxolane and 30–20% propylene glycol monomethyl ether, with continuous stirring at 700 rpm at room temperature for 3 h. Initially, N-methyl-2 pyrrolidone (NMP) based solvents such as J. T. Baker® PRS™-3000, Remover PG (MicroChem), and filtered NMP (Ultra Pure Solutions, Inc.) were used for liftoff; however, those solvents react with GeTe. In fact, J. T. Baker® PRS™-3000 etches the GeTe in just a few seconds. Remover PG and filtered NMP oxidize the surface, which can be observed with naked eye as discoloration of the GeTe surface from silvery color to dark brown color. Filtered NMP has a lesser impact among NMP-based solvents but can still oxidize GeTe. Therefore, EBR PG solvent was used for metal liftoff. The XPS core level of the Te 3d5/2 of samples treated with Remover PG and EBR PG compared to the as received sample is shown in Figure 2.3. Oxidation of GeTe modifies the crystallization temperature of GeTe and consequently the performance of the GeTe-based switch50.
Figure 2.3: XPS spectra of Te3d_{5/2} of GeTe (a) degreased, (b) dipped in Remover PG heated at 60°C for 10 min, and (c) dipped in EBR PG for 1hr. Remover PG clearly oxidizes the sample. (Instrumental and data analysis details of XPS are reported in section 2.5.)

For the mesas, a tri-layer of PMMA A6 950/LOR A5/SPR3012 resist stack was used to avoid O₂ plasma ashing, which is an unpredictable and time-consuming process.
The detailed description of the 2\textsuperscript{nd} stage of photolithography (mesas fabrication) is listed below:

1. Dehydration bake on hot plate at 115 °C for 3 min and cool for 1 min.
2. Spin-coat with PMMA A6 950 at 5 krpm for 45 s (350 nm thick).
3. Bake on hot plate at 180 °C for 3 min, then cool for 2 min.
4. Spin-coat with LOR 5A at 6krpm for 45 s (400 nm thick).
5. Bake on hot plate at 180 °C for 2 min, and cool for 2 min.
6. Spin-coat sample with SPR 3012 at 4.5 krpm for 45 s and bake on hot plate at 95 °C for 60 s (1.2 µm thick).
7. Expose for 0.39s using the GCA 8000 i-line Stepper.
8. Develop using CD-26 developer for 55 sec and rinse using DI H$_2$O, dry with N$_2$.
9. Inspect using optical microscope.
10. Flood with DUV for 30 min.
11. Develop in toluene for 60s and rinse with DI H$_2$O, dry with N$_2$.
12. Inspect using optical microscope.

A Cl$_2$ dry etch is used to isolate the GeTe mesas for 17 s in a Plasmatherm Versalock 700PECVD system. Afterwards, the masas masks are removed in EBR PG for 3 h. The final mesa edges are $< 0.5$ µm wider than the metal pads on either side. Figure 2.4 shows a SEM micrograph of a complete RTLM structure set with gap spacing varying between 20–0.6 µm.
Figure 2.4: SEM Micrographs of a complete set of RTLM structures. Inset is a magnified image of the pair of contacts with the 1.2 μm gap.

2.5 X-ray Photoelectron Spectroscopy Surface Analysis

Samples were immediately loaded into the XPS vacuum system (within 5 min of the treatment). The XPS spectra were collected by Dr. Hamed Simchi. The XPS spectra were acquired using a VersaProbe II Physical Electronics with a monochromatic Al Kα x-ray excitation using an applied voltage of 20 kV with a takeoff angle of 54° relative to the sample surface. The X-ray beam spot size was 200 μm in diameter. Ge 2p3/2, Te 3d5/2, S 2p, and Cl 2p spectra were collected together with the C 1s and O 1s peaks. The analysis was performed with a pass energy of 23.5 eV. An Ar⁺ ion gun (1 keV, 15mA) was used to perform GeTe surface etching (simulating Ar⁺ plasma treatment). For the data analysis, deconvolution of the spectra was performed in CasaXPS (Casa Software Ltd., version 2.3.15). Charging corrections were calculated with the C 1s peak at 284.6 eV (adventitious carbon peak) as the reference except for the Ar⁺ ion etching treatment, wherein the Ge⁰ component of the Ge 2p3/2 at 1217.7 eV was used rather than the C 1s due to the absence of the later peak after Ar⁺ ion etching. The background due to inelastic scattering was subtracted using Shirley method⁵¹. Peaks were fit with Gaussian-Lorentzian curves satisfying the following constraints: a) the doublet intensities have the ratio of 3:2 and 2:1
for the electrons from d and p orbitals, respectively; b) each doublet has equal full width at half maximum (FWHM); and c) the spin orbit splitting of the doublets is matched with the database\textsuperscript{52,53}. In each case, the residual standard deviation used to evaluate the difference between the actual data and fit envelope were also minimized to get the best fit.

2.6 Contact Resistance Measurements via Transfer Length Method

2.6.1 Electrical Measurements

For electrical measurements, a four-point probe technique was used to measure the total resistance ($R_T$) for each gap using a Keithley 238 parameter analyzer with linear current sweep and voltage measurement. For each gap, the measured resistance was calculated between -100 to +100 mA. Figures 2.5a and 2.5b show the CTLM and RTLM measurement setup to measure the $R_T$ for each gap, respectively. Every specific contact resistance ($\rho_c$), and contact resistance ($R_c$) value reported in this thesis is an average value calculated from at least four different CTLM or RTLM sets. For all samples used in this thesis, at least four different RTLM sets are measured. Gap spacings and mesa widths of the test structures were measured using SEM.

![Figure 2.5: $R_T$ measurement setup of (a) CTLM, and (b) RTLM test structures.](image-url)
2.6.2 Contact Resistance Extraction

After the total resistance is measured for each gap, CTLM data points were fitted using the Levenberg-Marquardt method using four modified Bessel functions to extract the semiconductor sheet resistance (R_{sh}) and the transfer length (L_T) to calculate ρ_c as described by Marlow et al.\textsuperscript{54} and Ahmed et al.\textsuperscript{55}:

$$R_T = \frac{R_{sh}}{2\pi} \left[ \ln \left( \frac{d + r_0}{r_0} \right) + \frac{L_T}{r_0} I_0 \left( \frac{r_0}{L_T} \right) + \frac{L_T}{d + r_0} K_0 \left( \frac{(d + r_0)/L_T}{L_T} \right) \right]$$ \hspace{1cm} (2.1)

where R_T is the total resistance, d is the gap spacing, r_0 is the radius of the inner contact pads (r_0 = 40 µm), and I_0, I_1, K_0, and K_1 are modified Bessel functions. The transfer length is defined as the length over which most of the majority of the current is transferred\textsuperscript{44}:

$$L_T = \frac{\rho_c}{R_{sh}} \sqrt{d}$$ \hspace{1cm} (2.2)

RTLM data points were fitted using the linear least squares method using\textsuperscript{44}:

$$R_T = \frac{R_{sh} d}{Z} + 2R_c = \frac{R_{sh}}{Z} \left( d + 2L_T \right)$$ \hspace{1cm} (2.3)

where Z is the metal contact width (Z=25 µm). Figure 2.6 shows the extraction of R_c, R_{sh}, and L_T values from plots of R_T versus d.

![Figure 2.6: Extraction of R_c, R_{sh}, and L_T from the total resistance (RT) versus gap spacing plot of RTLM test structures (adapted from Schroder)\textsuperscript{44}.](image-url)
2.6.3 CTLM Vs RTLM Test Structures

To investigate the influence of different surface preparations, metal selection, and annealing on the specific contact resistance of very low resistance contacts, accurate measurements are imperative. For very low specific contact resistances ($\rho_c < 10^{-8} \ \Omega \cdot \text{cm}^2$), the effect of the metal sheet resistance cannot be ignored. For (Ni/Ti/Pt/Au) contact, the metal stack sheet resistance is 0.34 $\Omega/\square$. This metal sheet resistance could introduce a non-negligible error causing an over- or underestimation of $\rho_c$; hence, it must be controlled for reliable measurements. Using CTLM would give inaccurate values due to this metal resistive contribution to the measurements. Therefore, RTLM test structures, as used by Dormaier$^{56}$, are employed in this thesis to minimize these errors.

However, $\rho_c$ of metal contacts to GeTe reported by Chua et al.$^{38}$ were extracted using CTLM test structures, which we think is not the most accurate method to extract the contact resistances of low sheet resistance semiconductors. Hence, we fabricated the CTLM structures to compare them with the RTLM structures. CTLM and RTLM test structures are fabricated to measure the contact resistance of Ni/Ti/Pt/Au (30/15/15/100 nm) contacts using two different surface preparation procedures: Ar$^+$ plasma and (NH$_4$)$_2$S, as described in section 2.2. Figure 2.7 illustrates a comparison between the $\rho_c$ extracted from RTLM and CTLM test structures. The RTLM values are one order of magnitude higher than the CTLM corresponding values. Also, using CTLM, $\rho_c$ even lower is achieved than that reported by Chua et al.$^{38}$ (who used CTLM structures and the Ar$^+$ plasma preparation prior to 30 nm Ni/150 nm Al metallization).
Figure 2.7: The specific contact resistances and corresponding surface preparations for CTLM and RTLM test structures.

Using CTLM, an over- and underestimation of $\rho_c$ is experimentally encountered in this work. Figure 2.8 shows dependence of $\rho_c$ on the probe position of four different configurations. Therefore, RTLM will be adopted for specific contact measurements on GeTe in this thesis.
Figure 2.8: Probe position dependent problem encountered in CTLM test structures.
2.7 Thermal Stability

2.7.1 Thermodynamic Calculations

2.7.1.1 Introduction

Thermally stable contacts to GeTe are crucial for PCM-based devices, just as low contact resistance is. The contacts will be subjected to heat treatment during device processing and packaging, as well as modest heating during switching. To avoid reaction when the contact is heated, a contact in thermodynamic equilibrium with GeTe could be chosen. On the other hand, reactions might lower the contact resistance if one is able to control them. Ternary phase diagrams of metal-Ge-Te systems are very useful tools in identifying the most thermodynamically stable metal contacts to GeTe. Hence, M-Ge-Te (M= Ni, Au, Mo) isothermal ternary phase diagrams were calculated at room temperature (298 K) based on the TerQuat method described by Klingbeil and Schmid–Fetzer. This work is concerned about α-GeTe since the films used in this study contain this phase. We have calculated the ternary phase diagrams at room temperature with and without suppressing the formation of the γ-GeTe phase, which is thought by some researchers to be an equilibrium phase, but its formation is very slow (kinetically hindered).

2.7.1.2 Past Studies on M-Ge-Te Systems

Few ternary compounds were reported for the selected metals in this work and GeTe. A Ni$_{5.45}$GeTe$_2$ ternary phase with tetragonal crystal structure (space group: I4/mmm) was reported for by Deiseroth *et al.*; however, no thermodynamic data was reported. More recently, an attempt to dope (alloy) GeTe with Ni was carried to enhance the thermal stability of GeTe and consequently the switching properties. However, no thermodynamic data was presented. Prince *et al.* reported that Au is in thermodynamic equilibrium with Ge and α-GeTe at temperatures below 375 °C.
2.7.1.3 Estimation of Metal-Ge-Te Isothermal Ternary Phase Diagrams

In order to calculate an isothermal ternary phase diagram, the entropy of formation ($\Delta S_f^\circ$) and enthalpy of formation ($\Delta H_f^\circ$) for each of the equilibrium binary compound are compiled. Afterwards, the Gibbs free energy of formation ($\Delta G_f^\circ$) for each binary compound is calculated using the following equation

$$\Delta G_f^\circ = \Delta H_f^\circ - \Delta S_f^\circ T$$ (2.4)

In each system, all possible tie-lines are identified. Then, comparing the Gibbs free energy of reaction ($\Delta G_{\text{run}}^\circ$) between any selected four different binary phases (2 phases as reactants and the other 2 as products) yields a possible stable tie-line that competes with all other possible stable tie-lines to yield the most stable tie-line; hence, it is chosen and represented by a solid line. The Gibbs free energy of reaction is always negative for any possible reaction involving two certain product phases connected with stable tie-line. In addition, all alternative tie-lines are taken into the account when a tie-line is calculated to be unstable by less than 8 kJ/(mol of atoms) and represented by a dashed line.

Due to limited available thermodynamic data in the literature for the Gibbs free energy of formation of the $\gamma$-GeTe phase and because the formation of $\gamma$-GeTe may be suppressed, the ternary phase diagrams were calculated for each metal with and without the separation of the $\gamma$-phase. The enthalpy and entropy of formation of $\alpha$-GeTe tabulated by Kubaschewski were used for ternary phase diagrams calculation with the suppression of $\gamma$-GeTe phase $\Delta H_f^\circ = -24.3\text{kJ} / (\text{mol of atoms})$ and $\Delta S_f^\circ = 4.2\text{J} / \text{K}\cdot\text{mol of atoms}$.

There is no experimental $\Delta H_f^\circ$ or $\Delta S_f^\circ$ reported for $\gamma$-GeTe; however, Schlieper et al. modeled the Ge-Te system binary phase diagram by compiling all the literature for other phases in the system and proposed new optimized thermodynamic values that match the phase diagram. Hence, we used the Gibbs free energy, enthalpy, and entropy of formation for both the GeTe phases using those values as tabulated in Table 2.3 in a second set of calculations. Those values will be used to calculate the ternary phase diagrams without the suppression of $\gamma$-GeTe. It might not be as accurate to compare the experimental value of $\alpha$-GeTe with the modeled $\gamma$-GeTe phase.
The selection of binary phases included in the calculations is made using binary phase diagrams and the literature. One special case is the Ni$_{0.8}$Te intermetallic phase in the Ni-Te system. The Ni-Te system has three intermediate compounds: Ni$_{1.43}$Te, Ni$_{1.29}$Te, and Ni$_{0.8}$Te. The Ni$_{0.8}$Te compound is a continuous solid solution extending over 14% of the phase diagram from NiTe$_{1.1}$, which has a hexagonal crystal structure (NiAs type), to NiTe$_2$ (CdI$_2$ type) which is closely related to the NiAs structure. Due to this large homogeneity, these solution phase was treated as two distinct compositions with different thermodynamic data, however, both compositions were in equilibrium with the same germanide (Ni$_2$Ge).

Most of the thermodynamic data are compiled from three main sources: Materials Thermochemistry by Kubaschewski, Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides by Mills, and Cohesion in Metals: Transition Metal Alloys by de Boer. Also, additional sources for thermodynamic data are used and cited in Table 2.3. If no experimental data for $\Delta H_f^o$ was found for metal germanides, then Miedema’s estimate was used as listed by de Boer. The selected binary phases and their $\Delta G_f^o$, $\Delta H_f^o$, and $\Delta S_f^o$ are listed in Table 2.3 with their references.

A few assumptions were taken into our calculation and should be noted:

1. Intermetallic phases were treated as line compounds.
2. Solid solubility is not treated in this calculation.
3. It was sometimes necessary because of a lack of available data to take the entropy of formation of phases to be zero, which is a reasonable assumption since the entropy of solids is very negligible.
4. The vapor pressure of Te$_2$ above GeTe is ignored because thermodynamic calculations determined that it is negligible at room temperature.

Also, the reader is reminded that these calculations were performed at room temperature, and therefore the phase diagrams could be different at the annealing temperatures. Nevertheless, the enthalpy term dominates the free energy calculation, and does not change much with temperature, so the solid-phase equilibria will not change that
much with moderate increases in temperature.

Table 2.3: Thermodynamic data used to calculate ternary phase diagrams.

<table>
<thead>
<tr>
<th>System</th>
<th>Phase</th>
<th>Enthalpy of formation (kJ/mol of atoms)</th>
<th>Entropy of Formation (J/K.mol of atoms)</th>
<th>Gibbs free energy of formation (kJ/mol of atoms)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge-Te</td>
<td>α-GeTe</td>
<td>-24.3</td>
<td>4.2</td>
<td>-25.5</td>
<td>60</td>
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<tr>
<td></td>
<td>α-GeTe</td>
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<td>-8.35</td>
<td>32</td>
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<tr>
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<td>γ-GeTe</td>
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</table>

2.7.2 Annealing GeTe

2.7.2.1 Annealing Vs Gap Spacing

Upon annealing, changes in the GeTe microstructure were observed. The cracks characteristic depends on the annealing temperature and the metal used and will be discussed in details in Chapters 4-6. Figure 2.9 illustrate a comparison between the $R_T$ vs gap spacing fitting for Ar⁺ plasma-treated Au (100 nm) contact before and after annealing 350 °C for 30 min. An anomaly on the large gaps is observed after annealing, affecting the extraction of $R_c$, $\rho_c$, and $R_{sh}$ (Figure 2.6).
Figures 2.9: $R_T$ vs gap spacing fitting for $Ar^+$ plasma-treated Au (100 nm) contact to GeTe (a) as-deposited and (b) after annealing.

Figures 2.10a-d illustrate the different impact of annealing at 350 °C for 30 min on different gap spacings: 8 µm and 2 µm for the Mo/Ti/Pt/Au (5/15/15/100 nm) contacts. Gaps < 2 µm retained their structure compared to gaps > 2 µm, where the cracks evolved between the contacts impacting the I-V measurements. Note that for the contacts shown in Figures 2.10a-d, the mesa etch step was not performed to show the difference in the microstructure of the GeTe close to and far away from the metal pads and because the effect of annealing is more pronounced.

Figure 2.11 shows the different effect of annealing on different gap spacing in HCl-treated Ni/Ti/Pt/Au (30/15/15/100 nm) after annealing at 350 °C for 30 min. The change in the GeTe between the contacts is uniform only in small gaps. For large gaps the cracks concentration increase next to the metal edge and decrease in the middle of the channel. Therefore, only gaps ≤ 2 µm are used to extract $\rho_c$, $R_c$, and $R_{sh}$. The results of the large gaps are also reported in Appendix B, C, and D individually for each metal.
Figure 2.10: Cracks evolving in Ar+ plasma-treated Mo/Ti/Pt/Au (5/15/15/100 nm) contacts annealed at 350 °C for 30 min for (a) 8 µm gap, (b) 2 µm gap spacings. (C) and (d) show the same micrographs in (a) and (b), respectively, with dotted lines in the micrographs to aid viewing the two different GeTe microstructures after annealing.
Figure 2.11: SEM micrograph showing morphology changes in (a) 1 µm and (b) 16 µm of HCl-treated Ni/Ti/Pt/Au (30/15/15/100 nm) contacts annealed at 350 °C for 30 min. Notice that the mesa step was performed here.

2.7.2.2 Annealing Conditions

Contact thermal stability was examined at three different annealing temperatures (250, 300, and 350 °C) for 30 min each in Ar ambient for each metal. Samples were loaded in an ATS (Applied Test Systems, Inc.) furnace and purged with an Ar with flow rate of 0.1 mL/min during annealing. 15 min Ar purging intervals were introduced before and after annealing. Initially, a few samples were annealed at the mentioned temperatures and tested. However, decomposition of GeTe in the channel was encountered, especially at 350 °C. Also, serious metal morphology changes occurred due to the reaction of the GeTe in the
channel on the metal surface, which will be discussed for each metal individually in chapters 4-6. Hence, 10 nm of SiO$_2$ layer as a capping layer was incorporated to preserve the channel integrity during annealing. It is easy to poke the probe tips through this capping layer later for contact resistance measurements. When appropriate, SEM and energy dispersive spectroscopy (EDS) maps were taken after annealing.

2.7.2.3 SiO$_2$ Capping Layer

A SiO$_2$ capping layer (10 nm) was introduced to suppress the cracking phenomena and after observing accumulation of material downstream in the annealing tube due to evaporation of Te. Figures 2.12a and 2.12b show the effect of annealing on Mo/Ti/Pt/Au (5/15/15/100 nm) contacts without and with 10 nm SiO$_2$ capping layer, respectively. Using the SiO$_2$ capping layer reduces the concentration of cracks but does not prevent it entirely.

![Figure 2.12: The effect of annealing at 350 °C for 30 min on the 8 µm gap of Ar$^+$ plasma-treated Mo/Ti/Pt/Au (5/15/15/100 nm) contacts (a) without and (b) with 10 nm SiO$_2$ capping layer.](image)

2.8 Auger Electron Spectroscopy (AES)

Reaction depth of a variety of samples was studied using AES depth profiles. AES depth profiles were performed using a PHI 670 scanning Auger microprobe to determine the elemental composition of the samples.
2.9 X-ray Diffraction (XRD)

XRD allowed for structural identification of the phases upon annealing. XRD data were collected and analyzed by Nichole Wonderling and K. C. Kragh-Buetow. Grazing incidence x-ray diffraction (GIXRD) was performed using a PANalytical XPer Pro MPD theta-theta diffractometer. XRD data was analyzed using MDI Jade +9 Analysis software.

2.10 Transmission Electron Microscopy

In order to observe the metal/semiconductor interface, selected samples were used for cross-sectional transmission electron microscopy (XTEM) analysis after electrical characterization was completed. These samples were prepared and characterized by Shih-Ying Yu and Kayla A. Cooly. All samples were first sputter-coated with 1 µm of carbon as a protective layer. An FEI Quanta 3D 200 dual-beam focused ion beam equipped with a Ga ion source was used to lift-out and thin cross-sections from specific sites located near the semiconductor gap in the RTLM test structures. The transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images are primarily taken in the FEI Talos transmission electron microscope using an accelerating voltage of 200 kV. Energy dispersive spectroscopy (EDS) mapping for elemental composition assessment was acquired with a built-in Super X-EDS system in the Talos. Bright-field and high-angle annular dark-field (HAADF) images were taken as needed. Additionally, selected-area electron diffraction (SAED) and fast Fourier transform (FFT) patterns were acquired to provide phase information. An aperture size of 200 nm is used to collect all SAED pattern for GeTe samples in this work which is the smallest aperture limited by instrumentation. Finally, energy dispersive spectroscopy (EDS) was performed to assess elemental composition.
Chapter 3
XPS Surface Characterization of GeTe as a Function of Surface Preparation

3.1 Introduction

In many metal/semiconductor contact studies, different surface preparation procedures prior to metallization have been found to result in widely different contact resistance (R_c) values. Also, an oxide-free interface prior to metallization is believed by some people to be crucial for obtaining very low contact resistance values. Removal of the oxide can yield a clean and uniform interface. Passivation of the surface to prevent any subsequent oxidation is also frequently desirable. The GeTe surface is prone to oxidation in air starting with oxidizing Ge to GeO_2 followed by a slower Te oxidation to TeO_2. Optimal surface preparation procedures prior to the metallization of the Metal/GeTe contacts, which could play an important role in facilitating low R_c, are still being clarified. Chua et al. used in-situ Ar⁺ plasma pre-cleaning for 5 min to achieve low R_c using 50 nm Ni, W, or TiW, followed by 150 nm Al, as the metal contact to both crystalline and amorphous GeTe. The lowest ρ_c of 8.6 × 10⁻⁹ Ω.cm² was achieved for the as-deposited Ni/Al contact to crystalline GeTe, as measured using circular transfer length method (CTLM) test structures.

In this chapter, x-ray photoelectron spectroscopy (XPS) was used to characterize the GeTe surfaces after oxidation via UV-O_3, as well as in- and ex-situ pre-metallization surface preparation procedures and the stability of the resultant surfaces in air. Additionally, different surface treatments might alter the surface elemental composition differently; hence, the surface elemental composition was investigated.

3.2 Past Studies on GeTe Oxidation

Yashina et al. have investigated both clean and oxidized (10⁴ – 10¹⁵ L of O_2) surfaces of α-GeTe (111) using x-ray photoelectron spectroscopy (XPS) and
complementary quantum chemical calculations. After exposure to molecular oxygen, the surface oxidation starts via formation of an intermediate peroxide structure with the oxygen molecule being bonded to Ge only, followed by formation of a Ge-enriched thin layer of $\text{Ge}^{4+}_{1+\delta}\text{Te}^{0}_{1-\delta}\text{O}^{2-}_{2(1+\delta)}$ where $\delta$ ranges from 0 to 0.5. Afterwards, this layer grows in thickness up to 2.5 nm to trigger the oxidation of Te, giving the final oxidation product of $(\text{GeO}_2)_m + (\text{TeO}_2)_n$.

Gourvest and co-workers$^{50}$ have used parallel angle resolved XPS to investigate the amorphous GeTe surface after aging in ambient conditions from 10 min to 90 days, yielding the same results reported by Yashina$^{71}$. In addition, Deringer et al.$^{72}$ simulated adsorption of molecular and atomic oxygen on the $\alpha$-GeTe(111) surface via density-functional theory (DFT).

3.3 Results and Discussion

The surface of polycrystalline $\alpha$-GeTe film was studied by XPS after different surface treatments including in-situ Ar$^+$ ion etching, deionized (DI) water, ammonium sulfide $((\text{NH}_4)_2\text{S})$, and hydrochloric acid (HCl) in an effort to remove surface oxides and prepare the surface for metallization. UV-O$_3$ is used often to remove organic contaminants after lithography and prior to metallization. Therefore, UV-O$_3$ treatment was used first for 10 min prior to ex-situ surface treatments. The reader is reminded that the experimental specifications of the XPS data analyses and different surface preparations details are provided in section 2.4. A summary of surface preparation procedures examined in this work is listed in Table 3.1.
Table 3.1: Summary of surface treatments used in the XPS study.

<table>
<thead>
<tr>
<th>Preparation Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Degreasing: 5 min acetone, 5 min IPA, 5 min DI water, 15 s DI water rinse, N₂ dry</td>
</tr>
<tr>
<td>2 Degreasing, 10 min UV-O₃ treatment</td>
</tr>
<tr>
<td>3 Degreasing, 5 min Ar⁺ plasma</td>
</tr>
<tr>
<td>4 Degreasing, 10 min UV-O₃ treatment, 5 min DI water, N₂ dry</td>
</tr>
<tr>
<td>5 Degreasing, 10 min UV-O₃ treatment, H₂O:HCl (10:1) 2 min, 15 s DI water rinse, N₂ dry</td>
</tr>
<tr>
<td>6 Degreasing, 10 min UV-O₃ treatment, H₂O:(NH₄)₂S (100:1) 30 s, 15 s DI water rinse, N₂ dry</td>
</tr>
</tbody>
</table>

3.3.1 Representative Deconvolutions of Relevant XPS Species as a Function of Surface Preparations

Some carbon and oxygen were visible on the surface of most samples, originating from a combination of adventitious carbon, hydrocarbons and water absorbed on the surface during exposure to ambient conditions. Figures 3.1-3.7 show representative deconvolutions of the Ge 2p₃/₂, Te 3d₅/₂, O 1s, and C 1s XPS core level peaks after different surface treatments. In each figure, peak fitting is also shown revealing different oxidation states (chemical environments).

It should be noted that the Ge 2p₃/₂ peak has a much higher binding energy (~1218 eV) compared to Te 3d₅/₂ peak (~573 eV), and therefore is more surface sensitive due to the small mean free path for electrons with low kinetic energies. The sampling depth (d) in which 95% of all photoelectrons are scattered and detected can be calculated using the inelastic mean free path (λ), which is kinetic energy and element dependent, and the take-off angle (α)

\[ d = 3\lambda \sin \alpha \quad (3.1) \]

Approximated sampling depths of 2 nm and 5 nm were calculated using α = 54°, and λ of 0.85 nm and 2.06 nm for Ge 2p₃/₂ and Te 3d₅/₂ core levels, respectively. Furthermore, even though XPS is a surface-sensitive analytical technique, there is still significant contribution from the GeTe bulk in most of the data.
Figures 3.1a and 3.1b show the core level peaks of Ge 2p$_{3/2}$ and Te 3d$_{5/2}$, respectively, after degreasing the as-received GeTe samples in acetone, isopropanol, and DI water for 5 min each and then blowing them dry with compressed N$_2$. The peak fitting for Ge 2p$_{3/2}$ revealed that there are three different oxidation states corresponding to elemental Ge (Ge$^0$), GeTe (Ge$^{+2}$), and an oxidized component, GeO$_2$ (Ge$^{+4}$). The presence of the Ge$^0$ peak suggests that the films not only consist of GeTe crystallites but also elemental Ge phase, which might be located at grain boundaries\textsuperscript{75}. This is in agreement with the result of Jung \textit{et al.}\textsuperscript{76} who reported the presence of Ge$^0$ and Ge$^{+2}$ components in the deconvoluted Ge 3d peak. The existence of elemental Ge is also proven using cross-sectional transmission electron microscopy (XTEM) in the later chapters. On the other hand, Te 3d$_{3/2}$ (see Appendix A) and Te 3d$_{5/2}$ peak (Figure 3.1b) fitting resulted in two components assigned to Te$^{-2}$ (GeTe) and elemental Te$^0$. The latter component appearance can be attributed to surface oxidation of GeTe wafer to GeO$_2$ and oxidation of Te$^{-2}$ to Te$^0$ prior to usage\textsuperscript{71}. No detectable signs of Te oxide were observed.
The average Ge$^0$, Ge$^{+2}$, and Ge$^{+4}$ binding energies for all samples in this work are 1217.76 ± 0.04 eV, 1218.03 ± 0.05 eV, and 1221.01 ± 0.17 eV, respectively. The corresponding binding energies of Te$^0$, Te$^{-2}$, and Te$^{+4}$ are 572.92 ± 0.04 eV, 572.57 ± 0.1 eV, and 576.07 eV, respectively. Those values within the error margin are in good agreement with most reported values in the literature, as listed in Table 3.2. Results from Yashina et al.$^{70,71}$ are slightly different; this small discrepancy might be attributed to the high quality single crystal used in their study compared to our polycrystalline films.
Table 3.2: GeTe Ge 2p\textsubscript{3/2} and Te 3d\textsubscript{5/2} XPS peaks binding energies in comparison with literature data.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Binding Energy (eV)</th>
<th>Ge 2p\textsubscript{3/2}</th>
<th>Te 3d\textsubscript{5/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ge\textsuperscript{0}</td>
<td>GeTe</td>
</tr>
<tr>
<td>This work</td>
<td></td>
<td>1217.76 ± 0.04</td>
<td>1218.03 ± 0.05</td>
</tr>
<tr>
<td>71</td>
<td></td>
<td>1217.75</td>
<td>1219.16</td>
</tr>
<tr>
<td>70</td>
<td></td>
<td>1217.5 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td></td>
<td>1217.9</td>
<td>1219.9</td>
</tr>
<tr>
<td>78</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>79</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Extracted from Figure 5 from the reference.

3.3.1.1 Oxidation via UV-O\textsubscript{3}

GeTe was oxidized for 10 minutes using UV-O\textsubscript{3} treatment (Figures 3.2a-d). The results suggest that UV-O\textsubscript{3} grows mainly non-stoichiometric GeO\textsubscript{x} (x<2) and stoichiometric TeO\textsubscript{2}, which is a very different growth mechanism than that reported by both Yashina \textit{et al.}\textsuperscript{71} and Gourvest \textit{et al.}\textsuperscript{50}, wherein the oxidation of Ge\textsuperscript{+2} to the Ge\textsuperscript{+4} occurred before Te oxides form under molecular oxygen and air exposures, respectively. Oxidation using O\textsubscript{3}, which is more reactive than molecular O\textsubscript{2}, results in significant
oxidation of Te$^2$ to Te$^{+4}$ at the expense of oxidation of Ge$^{+2}$ to Ge$^{+4}$. Additionally, small GeO$_2$ and TeO$_y$ ($y<2$) peaks were observed, too.

No attempt was made to further deconvolute the O 1s peak because there is a large number of oxygen-containing species expected (GeO$_2$, GeO$_x$, TeO$_2$, TeO$_y$, hydroxides, hydrocarbons, and H$_2$O) that have peaks close to each other, making the deconvolution of the peak difficult. The overall C intensity shown in Figure 3.2d is very low compared to that of the degreased sample due to the ability of UV-O$_3$ to decompose organic molecules. Afterwards, the oxides were etched using four different surface treatments and will be discussed in the next section.

Figure 3.2: Representative deconvolutions of the (a) Ge 2p$_{3/2}$, (b) Te 3d$_{5/2}$, (c) O 1s, and (d) C 1s XPS core peaks after 10 min UV-O$_3$.

3.3.1.2 Oxide removal treatments

All surface treatments were effective in removing most of oxides on GeTe in
different ways and will be discussed one by one here.

3.3.1.2.1 In-situ Ar$^+$ Ion Etching

Etching oxidized GeTe surface with an Ar$^+$ ion gun for 5 min (Figures 3.3a-b) removes all of the oxides but leaves a very Ge-rich surface due to preferential sputtering of Te compared to Ge atoms. The sputter yield of bombardment with 1 keV Ar$^+$ ions of elemental Te is three times larger than that of elemental Ge,$^{80}$ resulting in Te depletion from the surface. A small O 1s signal was detected originating from hydroxides and H$_2$O species that left on the sample after Ar$^+$ etching in the XPS chamber (Figure 3.3c). Figure 3.3d shows no C peak was detected due to its removal by Ar$^+$ ion bombardment with the surface. Please note that for Figure 3.3d only, the background was not subtracted since the background is the only signal that was detected.

Figure 3.3: Representative deconvolutions of the (a) Ge 2p$_{3/2}$, (b) Te 3d$_{5/2}$, (c) O 1s, and (d) C 1s XPS core peaks after 10 min of UV-O$_3$ followed by 5min Ar$^+$ plasma etching.
Note that in-situ Ar\textsuperscript{+} ion etching in the XPS chamber was used to simulate the effect of using in-situ Ar\textsuperscript{+} plasma prior to metallization in the deposition chamber of the Ni, Mo, Au-based Ohmic contacts to GeTe, as will be discussed in chapters 4-6. In those samples, no UV-O\textsubscript{3} was used prior to the Ar\textsuperscript{+} plasma treatment; therefore, the effect of Ar\textsuperscript{+} ion etching was also studied after degreasing without using UV-O\textsubscript{3} treatment. The results are shown in Figure 3.4a-d and are similar to these in Figure 3.3.

Figure 3.4: Representative deconvolutions of the (a) Ge 2p\textsubscript{3/2}, (b) Te 3d\textsubscript{5/2}, (c) O 1s, and (d) C 1s XPS core peaks of degreased sample followed by 5 min in-situ Ar\textsuperscript{+} plasma etching.
3.3.1.2.2 DI Water

Immersing the sample after UV-O$_3$ treatment into DI water for 5 min removed all oxide peaks on the surface (Figures 3.5a and 3.5b) except a minor non-stoichiometric Ge oxide peak, which has a binding energy between that of the underlying bulk GeTe and the stoichiometric oxide. This oxide may form because of the brief, unintentional oxidation of the surface after treatment before loading the sample into the XPS vacuum chamber. In addition, no elemental Te$^0$ component was present. Compared to the degreased sample (which is rinsed in DI water after degreasing), neither GeO$_2$ nor elemental Te$^0$ components were observed, indicating the importance of UV-O$_3$ treatment prior to H$_2$O treatment. The overall C intensity of the water-treated sample was the lowest among all surface treatments (Figure 3.5d).

![Figure 3.5](image.png)

*Figure 3.5: Representative deconvolutions of the (a) Ge 2p$_{3/2}$, (b) Te 3d$_{5/2}$, (c) O 1s, and (d) C 1s XPS core peaks after 10 min of UV-O$_3$ followed by DI H$_2$O for 5 min.*
3.3.1.2.3 Hydrochloric Acid

HCl is very effective in removing oxide species from the surface (Figures 3.6a-d). A noticeable broadening of Te 3d<sub>5/2</sub> peak of the HCl-treated sample is observed. The deconvolution of the peak revealed the contribution of an elemental Te<sup>0</sup> component at the surface in addition to Te<sup>-2</sup> peak. No Cl 2p peak was detected. A small non-stoichiometric Ge oxide peak was detected in both Ge 2p<sub>3/2</sub> (Figure 3.6a) and O 1s (Figure 3.6c) XPS spectra that may appear because of the brief, unintentional oxidation of the surface after treatment before loading the sample into the XPS vacuum chamber.

Figure 3.6: Representative deconvolutions of the (a) Ge 2p<sub>3/2</sub>, (b) Te 3d<sub>5/2</sub>, (c) O 1s, and (d) C 1s XPS core peaks after 10 min of UV-O3 followed by (10:1) H<sub>2</sub>O:HCl for 120 s.
3.3.1.2.4 Ammonium Sulfide

As shown in Figures 3.7a-c, (NH₄)₂S is effective in removing most of the UV-O₃ generated oxides but not the stoichiometric GeO₂. Also, no S 2p peak was detected after treatment, indicating a lack of surface passivation by S. The presence of GeO₂ after (NH₄)₂S treatment suggests that (NH₄)₂S either removes only non-stoichiometric Ge oxides or that the treatment is oxidizing the Ge to GeO₂ by itself.

Figure 3.7: Representative deconvolutions of the (a) Ge 2p₃/₂, (b) Te 3d₅/₂, (c) O 1s, and (d) C 1s XPS core peaks after 10 min of UV-O₃ followed by (100:1) H₂O:(NH₄)₂S for 30 s.

To check these hypotheses, (NH₄)₂S treatment was used after HCl treatment, which removes all oxides prior to (NH₄)₂S treatment, and the result is shown in Figure 3.8. The appearance of the GeO₂ peak is clear evidence that (NH₄)₂S oxidizes Ge to Ge⁴⁺. It also subsequently etches it. The 110 nm thick GeTe immersed in (NH₄)₂S is etched away in approximately 40 min.
Figure 3.8: XPS core level Ge 2p\textsubscript{3/2} of UV-O\textsubscript{3} + HCl treatment compared to UV-O\textsubscript{3} + HCl + (NH\textsubscript{4})\textsubscript{2}S treatment with an evidence of the ability of (NH\textsubscript{4})\textsubscript{2}S to oxidize Ge to Ge\textsuperscript{4+}.

3.3.2 Stability in Air

In order to evaluate the possibility of surface passivation by different \textit{ex-situ} treatments, samples were left in air and analyzed after 1 and 12 h at ambient conditions as shown in Figure 3.9. Regrowth of GeO\textsubscript{2} was observed within 1 h of all treatments, although there was no clear sign of TeO\textsubscript{2}. This result indicates poor surface passivation of the GeTe surface, even with (NH\textsubscript{4})\textsubscript{2}S and it emphasizes the need for fast loading into the deposition chamber after \textit{ex-situ} treatments to minimize air exposure and avoid regrowth of surface oxides. After 12 h, both GeO\textsubscript{2} and TeO\textsubscript{2} were observed on the surface. This result is consistent with the study by Gourvest \textit{et al.}\textsuperscript{50} on the long-term oxidation of GeTe at room temperature. From Figure 3.9, one can see that after 12 h, the H\textsubscript{2}O and HCl-treated samples have grown slightly more TeO\textsubscript{2} than the (NH\textsubscript{4})\textsubscript{2}S-treated sample. The noticeable shift of the Te 3d\textsubscript{5/2} peak position to higher binding energy is due to the oxidation of Te\textsuperscript{2-} to Te\textsuperscript{0}, which has been reported along with oxidation of by Yashina \textit{et al.}\textsuperscript{71,70}.
3.3.3 Surface Elemental Analyses

To study the impact of different surface treatments on the surface stoichiometry, the total peak areas of different elements/components were compared to each other. Figure 3.10 shows the total peak area for the Te 3d\textsubscript{5/2} over that of the Ge 2p\textsubscript{3/2} as a function of surface treatment. Among all surface treatments, the HCl-treated sample shows the highest Te/Ge peak area ratio and also is the only treatment that has elemental Te\textsuperscript{0} on the surface.

Figure 3.9: XPS core spectra of Ge 2p\textsubscript{3/2} and Te 3d\textsubscript{5/2} of (a-b)H\textsubscript{2}O, (c-d) HCl, and (e-f) (NH\textsubscript{4})\textsubscript{2}S treatments as a function of time, respectively.
Figure 3.10: Total peak area of Te 3d\textsubscript{5/2}/Ge 2p\textsubscript{3/2} peaks as a function of surface treatment.

Figure 3.11 shows the elemental Ge\textsuperscript{0} component area over that of the total Ge 2p\textsubscript{3/2} peak area. The Ge\textsuperscript{0}/Ge peak areas ratio increases after Ar\textsuperscript{+} ion etching, DI water, and (NH\textsubscript{4})\textsubscript{2}S treatments. HCl treatment shows the opposite trend from the other treatment. One can conclude that, Ar\textsuperscript{+} ion etching, DI water, and (NH\textsubscript{4})\textsubscript{2}S treatments will alter the GeTe surface, resulting in Ge-rich surfaces compared to the HCl treatment that results in Te-rich surface.
Figure 3.11: Elemental Ge peak area over total Ge 2p\(_{3/2}\) peak area as a function of surface treatments.

3.4 Conclusions

Examination of several surface treatments for oxide removal, with the wet treatments performed after UV-O\(_3\) treatment, demonstrate that all treatments were effective at removing GeTe oxides. However, Ar\(^+\) ion etching, H\(_2\)O and (NH\(_4\))\(_2\)S modify the surface stoichiometry to a Ge-rich surface compared to HCl treatment, where the surface is Te-rich. (NH\(_4\))\(_2\)S treatment also oxidizes Ge and consequently etches the GeTe film. All treatments show poor stability in air, indicating a poor surface passivation following wet chemical treatments. In the next chapters, the impact of those surface treatments on contact resistance of different metals (Ni, Au, and Mo) contacts to GeTe will be clarified.
Chapter 4
Ni-based Ohmic Contacts to GeTe

4.1 Introduction

A very low ON-state resistance is required for phase change materials (PCM) based RF switches compared to the OFF-state. The contact resistance contributes significantly to the ON-state resistance, which impacts the switch performance. However, extremely low contact resistance to GeTe might be achieved with optimized surface preparation procedures, metal selection, and controlled interfacial reactions. Ni has a work function of 5.15 eV, the highest among all metals used in this study. The electron affinity of GeTe is 3.8 eV, which would provide a Schottky-Mott barrier height for an unreacted Ni/GeTe interface of -0.63 eV. Additionally, optimal surface preparation procedures, which could play an important role in facilitating low R_c of Ni-based contacts, are still being clarified. Chua et al. used in-situ Ar^+ plasma pre-cleaning to achieve low contact resistance values for Ni/Al (50/150 nm) contacts to both crystalline and amorphous GeTe. Low specific contact resistance (ρ_c) of 8.6 × 10^9 Ω.cm^2 was reported for the as-deposited Ni/Al contact to crystalline GeTe, as measured using circular transfer length method (CTLM) test structures. Note that the present work has addressed the error introduced by using CTLM test structures in measuring very low contact resistances in section 2.3.1.

Furthermore, thermally stable contact to GeTe is crucial for stable and long lifetime RF switches, just as low contact resistance is. Hence, metals that do not react or result in shallow reaction depths with semiconductor is favorable. The contacts will be subjected to heat treatment during device processing and packaging, as well as modest heating during the switching process. To avoid reaction when the contact is heated, a contact in thermodynamic equilibrium with GeTe could be chosen. Another way to lower the R_c is by controlled interfacial reactions. Reactions might lower the R_c if one is able to control them. The evolution of the Ni based contacts to crystalline GeTe as a function of annealing has not been fully explored. Chua et al. studied the effect of annealing on the amorphous GeTe but not the crystalline GeTe. Therefore, we wanted to start with metal that have been
studied as baseline of our processing.

Herein, we examine the performance of Ni/Ti/Pt/Au (30/15/15/100 nm) contacts to GeTe in terms of contact resistance and thermal stability. The impact of various surface preparation producers is examined. The stability of the Ni/Ti/Pt/Au (30/15/15/100 nm) contacts upon annealing and possible eventual failure mechanisms have been investigated.

4.2 Contact Resistance Results

4.2.1 $R_c$ as a Function of Surface Treatments

The trend of the as-deposited contact resistance ($R_c$) and specific contact resistance ($\rho_c$) as a function of different surface preparations used prior to metallization is shown in Figure 4.1a and 4.1b, respectively. Ar$^+$ plasma, DI H$_2$O and (NH$_4$)$_2$S treatments were found to provide lower contact resistances compared to HCl treatment for the as-deposited contacts. A measured $R_c$ of 0.014 ± 0.001 $\Omega$.mm, 0.013 ± 0.005 $\Omega$.mm, and 0.014 ± 0.002 $\Omega$.mm were found for Ar$^+$ plasma, H$_2$O, and (NH$_4$)$_2$S treatments, respectively. HCl treatment resulted in markedly higher $R_c$ (0.032 ± 0.003 $\Omega$.mm). Clearly, surface treatments affect the $R_c$ of Ni-based contacts. X-ray photoelectron spectroscopy (XPS) examinations of GeTe surfaces that have undergone identical surface preparations as the samples measured in this section were discussed in chapter 3. Treatments that resulted in lower $R_c$ also resulted in the Ge-rich surface prior to metallization. On the other hand, HCl surface treatment results in a Te-rich GeTe surface and has the highest $R_c$ among all treatments. This relatively higher $R_c$ might be associated with formation of a Ni-Te phase at the interface that is elaborated upon in section 4.3.1.2. A summary of the different surface preparation procedures used prior to Ni/Ti/Pt/Au (30/15/15/100 nm) contact metallization and the relevant extracted values are shown in Table 4.1.
Figure 4.1: (a) $R_c$ and (b) $\rho_c$ of as-deposited Ni/Ti/Pt/Au (30/15/15/100 nm) as a function of surface preparations procedures used prior to metallization.

Table 4.1: Summary of the extracted data from I-V measurements for the as-deposited Ni/Ti/Pt/Au (30/15/15/100 nm) contacts as a function of surface treatments. (Those values were extracted using gap spacings ≤ 2 μm. For more details, see Appendix B.)

<table>
<thead>
<tr>
<th>Surface treatment</th>
<th>$R_c$ (Ω.mm)</th>
<th>$\rho_c$ (Ω.cm$^2$)</th>
<th>$R_{sh}$ (Ω.□$^{-1}$)</th>
<th>$L_t$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar$^+$/plasma</td>
<td>0.014 ± 0.001</td>
<td>4.6 ± 1.4 × 10$^{-8}$</td>
<td>44.8 ± 1.7</td>
<td>0.31 ± 0.05</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.013 ± 0.005</td>
<td>4.8 ± 3.5 × 10$^{-8}$</td>
<td>47.3 ± 4.2</td>
<td>0.30 ± 0.13</td>
</tr>
<tr>
<td>(NH$_4$)$_2$S</td>
<td>0.014 ± 0.002</td>
<td>4.6 ± 1.6 × 10$^{-8}$</td>
<td>48.2 ± 2.8</td>
<td>0.30 ± 0.06</td>
</tr>
<tr>
<td>HCl</td>
<td>0.034 ± 0.003</td>
<td>2.5 ± 0.5 × 10$^{-7}$</td>
<td>47.4 ± 2.8</td>
<td>0.72 ± 0.08</td>
</tr>
</tbody>
</table>

4.2.2 $R_c$ as a Function of Annealing

Ni-based contacts undergo dramatic electrical and mechanical changes upon annealing. The impact of the annealing on $R_c$ of Ni-based contacts depends strongly on the annealing temperature. Different temperatures were investigated: 200, 250, 300, and 350 °C for 30 min after depositing a 10 nm SiO$_2$ capping layer to suppress the evaporation of Te. Several reliability problems occurred such as delamination of the Ti/Pt/Au metal pads...
and defect formation as a function of the annealing temperature.

### 4.2.2.1 Annealing at \( \leq 250 \, \text{oC} \)

In general, \( R_c \) increased upon annealing at temperatures \( \leq 250 \, \text{oC} \). However, the exact value of \( R_c \) could not be extracted due to the poor least square fitting of the resultant total resistance versus the gap spacing. Annealing at temperatures \( \leq 250 \, \text{oC} \) for 30 min results in the contact electrical failure. AES depth profile of \( \text{Ar}^+ \) plasma-treated Ni/Ti/Pt/Au (30/15/15/100 nm) contacts before and after annealing at 200 \( \text{oC} \) for 30 min are shown in Figures 4.2a and 4.2b, respectively. After annealing, Ni consumed almost the whole GeTe layer causing the \( R_c \) to increase drastically. In addition, annealing for longer time (> 30 min) will eventually led to the delamination of the Ti/Pt/Au metal barrier leaving reacted Ni-Ge-Te behind on the substrate.

![Figure 4.2](image)

**Figure 4.2:** AES depth profile of \( \text{Ar}^+ \) plasma-treated Ni/Ti/Pt/Au (30/15/15/100 nm) contacts (a) before and (b) after annealing at 200 \( \text{oC} \) for 30 min.

### 4.2.2.2 Annealing at 300 \( \text{oC} \)

Annealing at 300 \( \text{oC} \) for 30 min resulted in mechanical failure of the contact as shown in the optical image in Figure 4.3. Delamination of the Ti/Pt/Au metal barrier occurred and no electrical data could be collected at this temperature. Note that multiple samples were tested at this temperature, which all suffer from serious delamination of the
Ti/Pt/Au layer.

Figure 4.3: Optical image of the Ar+ plasma-treated Ni/Ti/Pt/Au (30/15/15/100 nm) contacts annealed at 300 °C for 30 min showing the delamination and folding of the Ti/Pt/Au layer.

4.2.2.3 Annealing at 350 °C

Annealing at 350 °C for 30 min resulted in different trends for different surface preparations. The HCl-treated sample shows a reduction in the $R_c$ after annealing. On the other hand, the (NH$_4$)$_2$S-treated sample shows a slight increase in the $R_c$, which might be attributed to delamination of the Ti/Pt/Au barrier and the changes GeTe under the contacts undergoes upon annealing. The trend in the $R_c$ of annealed HCl- and (NH$_4$)$_2$S-treated samples at 350 °C for 30 min is shown in Figure 4.4. Additionally, all samples suffered from slight delamination of the Ti/Pt/Au layer at the corners of the metal pads as shown in Figure 4.5. The delamination is somehow weaker than that at 300 °C.
Figure 4.4: $R_c$ of ($NH_4)_2S$ and HCl-treated Ni/Ti/Pt/Au (30/15/15/100 nm) contacts as a function of annealing temperature with SiO$_2$ capping layer.

Figure 4.5: Optical image of the ($NH_4)_2S$-treated Ni/Ti/Pt/Au (30/15/15/100 nm) contacts capped with 10 nm SiO$_2$ annealed at 350 °C for 30 min showing slight delamination and folding of the Ti/Pt/Au layer.
Figures 4.6a and 4.6b show the change in the GeTe microstructure between the contacts before and after annealing at 350 °C (without SiO$_2$ capping layer), respectively. Te volatilization from the GeTe film in the channel is observed after annealing as confirmed with energy dispersive spectroscopy (EDS) maps in Figure 4.7. Additionally, Auger electron spectroscopy (AES) data revealed the presence of Te on the metal pad surface. This result strongly suggests that volatilized Te from the exposed area of GeTe transported to the surface of the metal pad during annealing. Hence, a 10 nm SiO$_2$ capping layer was incorporated to prevent the evaporation of Te. Also, accumulation of material downstream in the annealing tube due to evaporation of Te was observed. However, the capping layer decreased the evaporation process but did not prevent it as shown in Figure 4.8. Formation of bubble-like defects and growth of telluride crystals at the metal edges were observed, which might be due to Te pressurizing under the capping layer, and it might be due to surface diffusion of Te. (Figure 4.9). A representative AES elemental map showing the distribution of Te around the edges of the metal pads is shown in Figure 4.10.

Figure 4.6: SEM micrographs showing the change in the GeTe microstructures (a) before and (b) after annealing at 350 °C for 30 min. The dark spots in (b) indicate the places where Te has been depleted.
Figure 4.7: EDS elemental maps of GeTe after annealing at 350 °C for 30 min. A stronger Si signal from the silicon nitride beneath the GeTe is evident where the GeTe is thinned or missing.

Figure 4.8: SEM micrographs showing the 1 µm gap annealed at 350 °C for 30 min (a) without and (b) with 10 nm SiO₂ capping layer. Notice the crystal growth along the metal edges in the capped sample.
Figure 4.9: SEM micrographs showing the telluride crystal growth at the metal pad edges of Ar\(^{+}\) plasma-treated Ni-based contact capped with 10 nm SiO\(_2\) upon annealing at 350 °C for 30 min.
4.3 EDS and TEM Characterization

4.3.1 As-Deposited

In order to better understand the role of the surface preparations and subsequently the interface stoichiometry on the $R_c$ of Ni-based contacts, cross-sectional transmission electron microscopy (XTEM) analysis was performed on the as-deposited in-situ Ar$^+$ plasma-, HCl-, and (NH$_4$)$_2$S-treated contacts. Also, the (NH$_4$)$_2$S-treated Ni contact was investigated after annealing at 350 °C for 30 min.

4.3.1.1 In-situ Ar$^+$ plasma Treatment

An XTEM bright field micrograph of the Ar$^+$ plasma-treated contacts is shown in Figure 4.11. Additionally, the corresponding high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) image, EDS map, and EDS line scan are shown in Figure 4.12. Slight Ni interdiffusion was observed at the interface before any intentional annealing.

Figure 4.10: SEM image of a metal pad and its representative AES O and Te maps showing the distribution of Te at the edges of the metal pad of an Ar$^+$ plasma-treated Ni-based contact capped with 10 nm SiO$_2$ upon annealing at 350 °C for 30 min.
Figure 4.11: Bright field XTEM image of Ar$^+$ plasma-treated Ni contacts to GeTe.

Figure 4.12: HAADF STEM image, EDS map, and line scan of the as-deposited Ar$^+$ plasma-treated Ni/Ti/Pt/Au (30/15/15/100 nm) contacts to GeTe.
4.3.1.2 HCl Treatment

Cross-sectional TEM bright field micrographs of the HCl-treated contacts are shown in Figures 4.13a-b, revealing the formation of a ~ 5 nm distinct layer at the interface. The HAADF STEM image and its corresponding EDS map and EDS line scan are shown in Figure 4.14 confirm the presence of a Ni-Te layer that is ~ 5nm thick. Moreover, Ni shows the ability to uniformly displace the native oxide of the Te-rich interface. The corresponding fast Fourier transform (FFT) pattern (Figure 4.13b inset) of the Ni-Te phase matches the Ni$_{1.29}$Te phase that has an orthorhombic crystal structure (Space group: Pnma)$^{82}$. The formation of the Ni$_{1.29}$Te layer is probably responsible for the accompanying increase in $R_c$ measured when the HCl preparation is used. It should be noted in the EDS map (Figure 4.14) the segregation of elemental Ge in the GeTe film, which is very consistent with the XPS result that showed the existence of the elemental Ge near the surface of the GeTe films. The EDS line scan data suggest that the HCl-treated sample interface has more oxygen than that of the Ar$^+$ plasma-treated sample, which is also very consistent with the XPS findings.

![Figure 4.13: (a) Bright field XTEM image, (b) HRTEM of the Ni/GeTe interface (inset shows the corresponding FFT of the squared area) of Ni/Ti/Pt/Au (30/15/15/100 nm) as-deposited contacts treated with HCl prior to metallization.](image)
Figure 4.14: HAADF STEM image, EDS map, and EDS line scan of the as-deposited HCl-treated Ni/Ti/Pt/Au (30/15/15/100 nm) contact.

The SAED patterns of the GeTe in the channel and under the contact for the as-deposited HCl-treated Ni/Ti/Pt/Au (30/15/15/100 nm) contact are shown in Figure 4.15a and 4.15b, respectively. The GeTe in the channel is polycrystalline with a preferred orientation. On the other hand, the GeTe under the contacts is polycrystalline with a wider variety of orientations. It seems like the metallization might induce some structural changes in the GeTe underneath it, which has been seen in many samples studied in this work. The GeTe that experienced HCl treatment is the least preferentially oriented of all examined
areas/samples in this work, with rings that are almost complete. Even so, a preferential orientation is still noticeable in the pattern.

Figure 4.15: SAED of the GeTe (a) in the channel region and (b) under the as-deposited HCl-treated Ni/Ti/Pt/Au (30/15/15/100 nm) contact.

4.3.1.3 (NH$_4$)$_2$S Treatment

Cross-sectional transmission electron microscopy (XTEM) images of (NH$_4$)$_2$S-treated Ni/Ti/Pt/Au (30/15/15/100 nm) contacts prior to annealing are shown in Figures 4.16a and 4.16b. The micrographs suggest fast intermixing of the Ni and GeTe layer. The STEM image and EDS map shown in Figures 4.17a and 4.17b, respectively, reveal the formation of ~20 nm of crystalline Ni-Ge-Te phase at the interface. FFT patterns revealed the existence of different phases in this layer through different diffraction patterns as the electron beam moves along the layer. However, those phases could not be identified. Formation of Ni$_x$Ge$_y$, Ni$_x$Te$_y$, and Ge$_x$Te$_y$ binary phases and Ni-Ge-Te ternary phases are possible. Again, the micrographs suggest the ability of Ni to displace surface oxides.
Figure 4.16: (a) Bright field XTEM micrograph of as-deposited (NH₄)₂S-treated Ni/Ti/Pt/Au (30/15/15/100 nm). (b) Bright field HRTEM micrograph showing the formation of a Ni-Ge-Te layer ~20 nm thick at the interface.

Figure 4.17: HAADF STEM image and EDS map of as-deposited (NH₄)₂S-treated Ni/Ti/Pt/Au (30/15/15/100 nm).
The SAED patterns of the GeTe in the channel and under the as-deposited \((\text{NH}_4)_2\text{S}\)-treated Ni/Ti/Pt/Au (30/15/15/100 nm) contact are shown in Figure 4.18a and 4.18b, respectively. In this case, we see a spot pattern from a few different grains between and under the contacts.

![SAED patterns](image)

*Figure 4.18: SAED of the GeTe (a) in the channel region and (b) under the as-deposited \((\text{NH}_4)_2\text{S}\)-treated Ni/Ti/Pt/Au (30/15/15/100 nm) contact.*

### 4.3.2 Annealed at 350 °C, 30 min

SEM micrograph of the \((\text{NH}_4)_2\text{S}\)-treated Ni-based contact annealed at 350 °C for 30 min and capped with 10 nm of SiO\(_2\) is shown in Figure 4.19a. It reveals the Ti/Pt/Au layer delamination at one of the metal pad corners. A low magnification cross-sectional TEM bright field micrograph of the sample is shown in Figure 4.19b, revealing the extensive reaction between Ni and almost the entire GeTe layer. The delamination of the Ti/Pt/Au layer is very obvious at the metal/semiconductor edge. Additionally, defects and holes evolve in the channel and between the reacted Ni-Ge-Te and the Ti/Pt/Au layer, leading to delamination of the latter, as clearly seen in Figure 4.19b and Figure 4.20. Also, defects and holes appear between the Si\(_3\text{N}_4\) and the Si substrate between the contacts, which might be due to annealing (Figure 4.19).
Figure 4.19: (a) SEM micrograph showing the peeling-off of the Ti/Pt/Au layer. (the dashed line show the place of the FIB cross-section). (b) Large-scale bright field XTEM of (NH₄)₂S-treated Ni/Ti/Pt/Au (30/15/15/100 nm) annealed at 350 °C for 30 min.

Figure 4.20: (a) Bright field XTEM micrograph of (NH₄)₂S-treated Ni/Ti/Pt/Au (30/15/15/100 nm) annealed at 350 °C for 30 min. (b) Bright field HRTEM micrograph showing the formation of a 5 nm Ni-Te layer at the interface.
Figure 4.21 shows the HAADF STEM image and EDS map of (NH$_4$)$_2$S-treated Ni/Ti/Pt/Au (30/15/15/100 nm) annealed at 350 °C for 30 min. The EDS map confirms the reaction between Ni and GeTe forming different binary phases (grains) of Ni$_x$Ge$_y$, Ni$_x$Te$_y$, and GeTe. Individual Ni, Te, and Ge EDS elemental maps are also shown in Figure 4.21. Ti, Pt, and Au stayed within their original respective layers. No lateral Ni diffusion into the channel was detected. No Ni signals were observed outside of the metal pad region.

In-situ Ar$^+$ plasma, H$_2$O, and (NH$_4$)$_2$S treatments resulted in almost the same low $R_c$ compared to the HCl treatment. HCl is the only treatment that resulted in surface rich in elemental Te. Having Te$^0$ at the metal/semiconductor interface triggered the formation of the Ni$_{1.29}$Te phase that is responsible for the large $R_c$ of the HCl-treated sample. On the other hand, formation Ni-Ge-Te phases at the interface of the (NH$_4$)$_2$S-treated sample resulted in lower contact resistance than that of the HCl treatment. One can conclude that
keeping Ge at the interface results in lower $R_c$. Moreover, it seems that having oxides at the interface is not that big of a problem for Ni-based contacts due to the ability of Ni to penetrate the surface oxides to react with the GeTe.

Annealing the HCl-treated sample at 350 °C for 30 min decreased the $R_c$ to almost match other treatments because upon annealing, Ni reacts with the entire GeTe layer and the Ni$_{1.29}$Te phase at the interface is no longer preserved. Additionally, regardless of the surface treatment used, upon annealing, the Ti/Pt/Au barrier is going to peel off when annealing at temperatures > 300 °C for 30 min or < 300 °C for longer time. Annealing a blanket sample of the contact resulted in the delamination of the Ti/Pt/Au layer as shown in Figure 4.22a. The peeling off of the barrier is concurrent with reaction of Ni with GeTe and formation of NiTe$_2$ phase. Grazing incidence x-ray diffraction (GIXRD) was conducted on the substrate shown in Figure 4.22a after the Ti/Pt/Au barrier peeled off upon annealing (Figure 4.22a). The GIXRD result suggests the formation of the NiTe$_2$ phase in addition to GeTe. The NiTe$_2$ phase is a metal with a layered structure (CdI$_2$ type)$^{83}$. The formation of this layered structure might be the reason behind the delamination of the Ti/Pt/Au layer.

The incorporation of Ni in GeTe led to serious reliability problems upon annealing. It is imperative to design not only low $R_c$ contacts to GeTe but also thermodynamically stable contacts that can sustain the required thermal load. Ni easily reacts with GeTe forming different phases at the interface at room temperature before any intentional annealing, which goes faster with annealing, giving rise to serious reliability problems.
4.4 Ni-Ge-Te Ternary Phase Diagram Calculation Results

The Ni-Ge-Te ternary phase diagrams from our thermodynamics calculation are shown in Figures 4.23a and 4.23b without and with the inclusion of the $\gamma$-GeTe phase, respectively. The ternary phase diagram suggests that reaction between Ni and GeTe is thermodynamically favored at room temperature. The equilibrium reaction products are NiTe$_2$ and NiGe as depicted in Figure 4.23a-b. NiTe$_2$ is a metal that has the CdI$_2$ layered structure$^{83,84}$. NiGe is metallic with the orthorhombic MnP-type structure$^{85}$ with a resistivity lower than Ni itself$^{86}$. The inclusion of the $\gamma$-GeTe phase did not alter the ternary phase diagram. It should be noted that there is a reported Ni-Ge-Te ternary phase (Ni$_{5.45}$GeTe$_2$)$^{58}$ that is potentially stable at the room temperature; however, there are no thermodynamic data available for this phase. The results of our calculation are consistent with the experimental results that show the extensive reaction of Ni with GeTe at room temperature.
Figure 4.23: Ternary phase diagrams of the Ni-Ge-Te system (a) without and (b) with the inclusion of the γ-GeTe phase in the calculation.

4.5 Conclusions

This section demonstrated that the $R_c$ of as-deposited Ni-based contacts to GeTe is very sensitive to the surface preparations used prior to the deposition of the contacts. Treatments that resulted in Ge-rich interfaces (*in-situ* Ar$^+$ plasma, H$_2$O, and (NH$_4$)$_2$S)) yielded lower $R_c$ values compared to the treatment that resulted in a Te-rich interface (HCl). The contact resistance values of the as-deposited Ni/Ti/Pt/Au (30/15/15/100 nm) contacts are relatively higher than those of the other metals studied in this thesis (Mo and Au in chapter 5 and 6, respectively). Although a negative barrier height is calculated using the Schottky-Mott model for an unreacted Ni/GeTe interface, and also reported by Chua *et al.*, TEM images have shown new phases formed at the interface as a function of the surface treatment. The higher contact resistance of as-deposited Ni-based contacts compared to those of Au and Mo might be attributed to the reaction between Ni and GeTe at room temperature, forming different phases at the interface. Ni-based contacts are not thermally stable and degrade electrically and mechanically upon annealing.

The use of Ni contacts to GeTe leads to serious reliability problems. Clearly, Ni is not the right answer, and a thermally stable contact with GeTe is needed. In the next two chapters, Au and Mo are suggested to be more promising metal contact candidates.
Chapter 5
Mo-based Ohmic Contacts to GeTe

5.1 Introduction

This chapter reports the results of our exploration of Mo-based contacts to GeTe in terms of contact resistance ($R_c$) and thermal stability upon annealing. Molybdenum has a relatively lower work function (4.6 eV) than Ni; however, it has a high melting point. The impact of different surface treatments, metal thicknesses, and annealing on $R_c$ was examined. The as-deposited Mo-based contacts consistently showed the lowest $R_c$ among all metals used in this thesis. The change in the $R_c$ upon annealing is explained in terms of interfacial reactions and metal-dependent characteristics.

5.2 Mo/Ti/Pt/Au Contacts

5.2.1 Contact Resistance as a Function of Surface Treatments

Three different surface treatments: in-situ Ar$^+$ plasma, (NH$_4$)$_2$S, and DI H$_2$O were used to study the role of the surface preparation procedures on Mo/Ti/Pt/Au (5/15/15/100 nm) contacts. The trend of the as-deposited $R_c$ ($\rho_c$) as a function of different surface preparations is shown in Figure 5.1a (5.1b). The results in Figure 5.1 suggest that Ar$^+$ plasma treatment produces lower $R_c$ compared to other treatments. Based on the XPS study discussed in Chapter 3, in-situ Ar$^+$ plasma treatment resulted in a Ge-rich surface with the depletion of Te from ~2 nm of the surface. Also, an almost oxide-free interface was produced with the Ar$^+$ plasma treatment, which might result in lower $R_c$ compared to other treatments. This result is different than that of the Ni contacts, where all treatments except HCl (which produced a Te-rich surface) showed almost the same $R_c$ ($\rho_c$), which might be due to the ability of Ni to displace the surface oxides at room temperature. The (NH$_4$)$_2$S and DI H$_2$O treatments prior to the metallization of the Mo-based contacts resulted in almost the same $R_c$ ($\rho_c$). Note that HCl treatment was not investigated due to the unsatisfying result from Ni-based contacts. Please note for this set of data, all gaps are used
to extract $R_c$ because some of the small gaps did not develop.

![Figure 5.1](image)

**Figure 5.1:** Dependence of (a) $R_c$ and (b) $\rho_c$ of as-deposited Mo/Ti/Pt/Au (5/15/15/100 nm) contacts on surface preparation procedures prior to metallization

A summary of the different surface preparation procedures of the as-deposited Mo/Ti/Pt/Au (5/15/15/100 nm) contacts to GeTe and their relevant extracted values are shown in Table 5.1.

**Table 5.1:** Summary of the extracted data from I-V measurements for the as-deposited Mo/Ti/Pt/Au (5/15/15/100 nm) contacts as a function of different surface preparation procedures, metal stacks, and metal thicknesses. (Those values were extracted using gap spacings $\leq 20 \mu$m. For more details, see Appendix C.)

<table>
<thead>
<tr>
<th>Metallization</th>
<th>Surface treatment</th>
<th>$R_c$ (Ω.mm)</th>
<th>$\rho_c$ (Ω.cm²)</th>
<th>$R_{sh}$ (Ω.μm⁻¹)</th>
<th>$L_t$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo/Ti/Pt/Au (5/15/15/100 nm)</td>
<td>Ar⁺ plasma</td>
<td>0.006 ± 0.001</td>
<td>7.9 ± 0.8 × 10⁻⁹</td>
<td>42.3 ± 0.6</td>
<td>0.14 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>0.008 ± 0.001</td>
<td>1.4 ± 0.2 × 10⁻⁸</td>
<td>44.3 ± 0.1</td>
<td>0.18 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>(NH₄)₂S</td>
<td>0.009 ± 0.001</td>
<td>2.0 ± 0.3 × 10⁻⁸</td>
<td>43.4 ± 0.3</td>
<td>0.21 ± 0.02</td>
</tr>
</tbody>
</table>
5.2.3 Contact Resistance as a Function of Annealing

The annealing study was conducted on the Mo/Ti/Pt/Au (15/15/15/100 nm) and Mo/Au (35/100 nm) contacts. No $R_c$ was extracted from the Mo/Au (35/100 nm) contacts due to the mechanical failure of the contacts upon annealing. Upon annealing, $R_c$ ($\rho_c$) of Mo/Ti/Pt/Au (15/15/15/100 nm) contacts slightly increased. Again, three different temperatures were investigated: 250, 300, and 350 °C for 30 min with and without 10 nm of SiO$_2$ capping layer to suppress the evaporation of Te (see section 2.7.2.3 for more details).

5.2.3.1 Contact Resistance as a Function of Annealing (Uncapped Contacts)

The $R_c$ ($\rho_c$) increased with increasing annealing temperature from $0.005 \pm 0.001 \Omega$.mm ($7.2 \pm 0.7 \times 10^{-9} \Omega$.cm$^2$) for the as-deposited contact to $0.009 \pm 0.001 \Omega$.mm ($2.0 \pm 0.4 \times 10^{-8} \Omega$.cm$^2$) after annealing at 350 °C for 30 min (Figures 5.2a-b). The Mo-based contact $R_c$ (0.009 ± 0.001) after annealing is still lower than the lowest values of the Ni-based contacts (0.013 ± 0.005), which might be due to the shallower Mo/GeTe reaction compared to Ni. The results are summarized in Table 5.2.

![Graphs](a) $R_c$ and (b) $\rho_c$ of Mo/Ti/Pt/Au (15/15/15/100 nm) contacts as a function of annealing temperature with and without SiO$_2$ capping layer.

Figure 5.2: (a) $R_c$ and (b) $\rho_c$ of Mo/Ti/Pt/Au (15/15/15/100 nm) contacts as a function of annealing temperature with and without SiO$_2$ capping layer.
5.2.3.2 Contact Resistance as a Function of Annealing (Capped Contacts)

The $R_c (\rho_c)$ increased upon annealing from $0.005 \pm 0.001 \, \Omega \cdot \text{mm} (7.2 \pm 0.7 \times 10^{-9} \, \Omega \cdot \text{cm}^2)$ to $0.009 \pm 0.002 \, \Omega \cdot \text{mm} (2.2 \pm 1 \times 10^{-8} \, \Omega \cdot \text{cm}^2)$ after annealing at 250 °C for 30 min, which is the highest $R_c (\rho_c)$ of capped Mo-based contacts after annealing (Figures 5.2a-b). Increasing the annealing temperature to 300 °C resulted in a decreased the $R_c (\rho_c)$ to $0.007 \pm 0.001 \, \Omega \cdot \text{mm} (1.3 \pm 0.4 \times 10^{-8} \, \Omega \cdot \text{cm}^2)$. Increasing the annealing temperature to 350 °C gave the same results as the annealing at 300 °C. Incorporation of a SiO$_2$ capping layer did not affect the results, and the small variation in $R_c (\rho_c)$ is due to sample-to-sample variation. The results are summarized in Table 5.2.

Table 5.2: Summary of the extracted data from I-V measurements for the annealed Mo/Ti/Pt/Au (15/15/15/100 nm) contacts as a function of annealing temperature. (Those values were extracted using gap spacings ≤ 2 µm. For more details, see Appendix C.)

<table>
<thead>
<tr>
<th>Annealing Temperature</th>
<th>$R_c$ (Ω.mm)</th>
<th>$\rho_c$ (Ω.cm$^2$)</th>
<th>$R_{sh}$ (Ω.Å$^{-1}$)</th>
<th>$L_s$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capped with 10 nm SiO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250 °C</td>
<td>0.009 ± 0.002</td>
<td>2.2 ± 1.0 × 10$^{-8}$</td>
<td>39.1 ± 2.9</td>
<td>0.23 ± 0.06</td>
</tr>
<tr>
<td>300 °C</td>
<td>0.007 ± 0.001</td>
<td>1.3 ± 0.4 × 10$^{-8}$</td>
<td>42.0 ± 2.7</td>
<td>0.17 ± 0.04</td>
</tr>
<tr>
<td>350 °C</td>
<td>0.007 ± 0.002</td>
<td>1.7 ± 0.9 × 10$^{-8}$</td>
<td>36.4 ± 1.1</td>
<td>0.21 ± 0.07</td>
</tr>
<tr>
<td>Uncapped</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250 °C</td>
<td>0.007 ± 0.002</td>
<td>1.3 ± 0.4 × 10$^{-8}$</td>
<td>41.0 ± 0.4</td>
<td>0.18 ± 0.03</td>
</tr>
<tr>
<td>300 °C</td>
<td>0.008 ± 0.001</td>
<td>1.7 ± 0.2 × 10$^{-8}$</td>
<td>39.9 ± 0.7</td>
<td>0.21 ± 0.02</td>
</tr>
<tr>
<td>350 °C</td>
<td>0.009 ± 0.001</td>
<td>2.0 ± 0.4 × 10$^{-8}$</td>
<td>40.1 ± 0.8</td>
<td>0.23 ± 0.02</td>
</tr>
</tbody>
</table>

5.2.4 Morphological Characterization

Upon annealing, slight changes in the GeTe microstructure were observed. Figure 5.3 shows different SEM micrographs for different conditions. The cracks after annealing at 350 °C for 30 min become deeper and more well defined (Figures 5.3b-c) compared to the as-deposited case (Figure 5.3a). It should be noted that characteristics of the cracks
after annealing depend on the metal contact to GeTe. Reaction of Te and/or Ge upon annealing on the metal surface is observed if the sample is not capped with SiO$_2$ (Figure 5.3c).

![SEM micrographs showing the slight difference in the GeTe microstructure and the contact (a) before annealing and after annealing at 350 °C for 30 min (b) with and (c) without the 10 nm SiO$_2$ capping layer. Notice the crystal growth along the metal edges in the capped sample.](image)

**Figure 5.3:** SEM micrographs showing the slight difference in the GeTe microstructure and the contact (a) before annealing and after annealing at 350 °C for 30 min (b) with and (c) without the 10 nm SiO$_2$ capping layer. Notice the crystal growth along the metal edges in the capped sample.

### 5.2.5 XTEM and EDS Characterization

#### 5.2.5.1 As-Deposited

#### 5.2.5.1.1 Ar$^+$ plasma treatment

A cross-sectional transmission electron microscopy (XTEM) image of an Ar$^+$ plasma-treated Mo/Ti/Pt/Au (15/15/15/100 nm) contact prior to annealing is shown in Figure 5.4. The micrograph suggests no serious reaction or diffusion of Mo into GeTe or
vice versa, at least based on the resolution of the data. The scanning transmission electron microscopy (STEM) image and the energy dispersive spectroscopy (EDS) map shown in Figures 5.5a and 5.5b, respectively, support the lack of reaction of Mo-based contacts at room temperature. Furthermore, the EDS line scan shown in Figure 5.6a supports the lack of reaction at the Mo/GeTe interface at room temperature.

![Figure 5.4: Bright field XTEM image of the as-deposited Ar$^+$ plasma-treated Mo/Ti/Pt/Au (15/15/15/100 nm) contacts to GeTe.](image)

![Figure 5.5: (a) HAADF STEM image, and (b) EDS map of the as-deposited Ar$^+$ plasma-treated Mo/Ti/Pt/Au (15/15/15/100 nm) contacts to GeTe.](image)
Figure 5.6: EDS line scans of Ar$^+$ plasma-treated Mo/Ti/Pt/Au (15/15/15/100 nm) contacts (a) as-deposited and (b) annealed at 350 °C for 30 min.

A low magnification cross-sectional HAADF STEM image of the same contact is shown in Figure 5.7a. Similar to the as-deposited Ni-based contacts, the GeTe between the contacts had a clear preferred orientation, as seen in the selected area electron diffraction (SAED) pattern in Figure 5.7b. However, the GeTe under the contacts was more randomly oriented, since the ring structure was more complete (Figure 5.7c). The change of the crystallinity under the contact may be attributed to metallization induced deformations.
5.2.5.2 Annealed at 350 °C, 30 min

In order to better understand the impact of annealing on the Mo/Ti/Pt/Au (15/15/15/100 nm) contacts, TEM was performed. Figure 5.8a shows a HAADF STEM image of a Mo/Ti/Pt/Au (15/15/15/100 nm) contact capped with 10 nm of SiO₂ and annealed at 350 °C for 30 min. There was considerable delamination under the channel, and the GeTe/Si₃N₄ layer was observed to be bent in an arch shape that might either
originate from FIB preparation or annealing. However, we acknowledge that annealing at 350 °C for 30 min is a very harsh condition that is unlikely to happen in actual operation/processing of the device. Additionally, a few voids were observed in the GeTe film at the Si₃N₄ interface after annealing.

Figure 5.8: HAADF STEM image of Mo/Ti/Pt/Au (15/15/15/100 nm) contact capped with 10 nm of SiO₂ and annealed at 350 °C for 30 min.

XTEM bright field micrographs are shown in Figure 5.9. HAADF STEM image and EDS map are shown in Figures 5.10a and 5.10b, respectively. The result suggests that Mo did not react deeply with the GeTe. However, upward diffusion of Ge and Te into the Mo layer is suggested, as seen in the extended tails of the Ge and Te EDS line into the Mo layer, as shown in in Figure 5.6b. No significant intermixing at any of the barrier metals Ti/Pt/Au was observed. The TEM results from the annealed sample indicated a little diffusion of Ge and Te into the Mo layer, corresponding to the slight degradation of contact resistance of Mo/Ti/Pt/Au (15/15/15/100 nm) after annealing. Additionally, an oxygen peak is observed to accompany the Ti layer in all Ar⁺ plasma-treated samples due to slight
oxidation of Ti during deposition, which might have been boosted by cooling the substrate during deposition. Additionally, it might be because of the poorer vacuum in the deposition system with the Ar\(^+\) plasma or lack of gettering with Ti prior to metallization, which we were able to do in other deposition systems.

![Image](image.jpg)

**Figure 5.9:** Bright field XTEM image of the Ar\(^+\) plasma-treated Mo/Ti/Pt/Au (15/15/15/100 nm) contacts to GeTe annealed at 350 °C for 30 min.

![Image](image.jpg)

**Figure 5.10:** (a) HAADF STEM image, (b) XEDS map of the annealed Ar\(^+\) plasma-treated Mo/Ti/Pt/Au (15/15/15/100 nm) contacts.

As seen in the capped Ni-based contacts after annealing, the capped Mo-based contacts show formation of small particles around the edges of the metal pads when the Ar\(^+\) plasma-treated Mo/Ti/Pt/Au (15/15/15/100 nm) contacts were annealed at 350 °C for
30 min with the 10 nm SiO$_2$ capping layer (Figure 5.11a). We used the term “particle” here instead of crystals because we could not judge the particle crystallinity as in the Ni contacts case, where the crystal planes were so obvious even in the SEM micrographs. Figure 5.11b is a STEM image showing the edge of the contact and the formation of telluride particles on top of the metal pads. The elemental analysis of the particles revealed that they were mainly composed of Te, Ge, and Pt (Figure 5.11c). The Cu and Al peaks could be from the grid or holder.

Figure 5.11: (a) SEM micrograph showing telluride particle growth at the metal pad edges of Ar$^+$ plasma-treated Mo/Ti/Pt/Au (15/15/15/100 nm) contacts annealed at 350 °C for 30 min with 10 nm SiO$_2$ capping layer. (b) Cross-sectional HAADF STEM image of the same contact showing the edge of the contact and the formation of telluride particles on the metal pads. (c) Elemental analysis of the particle in (b) (squared area).
5.3 Mo/Au (35/100 nm) Contacts

5.3.1 Contact Resistance as a Function of Surface Treatments

In an attempt to reduce the metallization processing time and avoid using metals that heat the chamber when they are evaporated, such as Pt, the Ti/Pt (15/15 nm) barrier was taken out. Au has a maximum solubility of about 1.25 at.% Mo at 1055 °C\textsuperscript{87}. Table 5.3 summarized the contact resistance and related parameter of Mo/Au (35/100 nm) contacts for two different surface preparation procedures.

Table 5.3: Summary of the extracted data from I-V measurements for the as-deposited Mo/Au (35/100 nm) contacts as a function of different surface preparation procedures. (Those values were extracted using gap spacings ≤ 20 μm. For more details, see Appendix C.)

<table>
<thead>
<tr>
<th>Metallization</th>
<th>Surface treatment</th>
<th>(R_c) (Ω.mm)</th>
<th>(\rho_c) (Ω.cm(^2))</th>
<th>(R_{sh}) (Ω.(\square^{-1}))</th>
<th>(L_t) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo/Au (35/100 nm)</td>
<td>H(_2)O</td>
<td>0.008 ± 0.001</td>
<td>1.7 ± 0.6 \times 10^{-8}</td>
<td>41.4 ± 2.7</td>
<td>0.20 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>(NH(_4))(_2)S</td>
<td>0.007 ± 0.003</td>
<td>1.4 ± 1.4 \times 10^{-8}</td>
<td>43.8 ± 5.2</td>
<td>0.16 ± 0.09</td>
</tr>
</tbody>
</table>

However, Mo/Au (35/100 nm) contacts failed mechanically upon annealing because a new type of defect emerged in the contact. The defects have a bubble-like appearance as shown in Figures 5.12a-b. The bubbles grew in different sizes up to 130 μm in diameter and 5 μm in height. The formation of those defects can be attributed to Te out-gassing and buckling of the Mo/Au layer during annealing. Perhaps the metallization layer blocks the Te out-gassing from the GeTe layer. This observation emphasizes the need for the Ti/Pt/Au barrier in the Mo-based contacts.
5.4 Mo-Ge-Te Ternary Phase Diagram Calculation Results

The resulting Mo-Ge-Te ternary phase diagrams of our thermodynamic calculations are shown in Figures 5.14a and 5.14b without and with the inclusion of the $\gamma$-GeTe phase, respectively. The experimental thermodynamic data (Figure 5.14) suggests that reaction between Mo and GeTe is thermodynamically favored at room temperature if the kinetics permits and that Mo$_5$Ge$_3$ and MoTe$_2$ are in thermodynamics equilibrium with GeTe at room temperature. MoTe$_2$ is a semiconductor with the cadmium chloride layer structure$^{83,84}$. Mo$_5$Ge$_3$ has tetragonal crystal structure (W$_5$Si$_3$ type)$^{85}$ and no electrical properties are reported.

On the other hand, the assessed thermodynamic data (Figure 5.14b) suggest that GeTe is in thermodynamic equilibrium MoTe$_2$, but is not in equilibrium with any metal germanides. It should be noted that the inclusion of the $\gamma$-GeTe phase in the case of Mo yielded a different diagram. It is not surprising, since the thermodynamic data were taken from two different sources with significant difference in the thermodynamic parameters.
5.5 Conclusions

Mo-based contacts show both low $R_c$ and thermal stability; hence, they are promising candidates as metal contacts to RF switches made from GeTe. The measured contact resistance values for the Ar$^+$ plasma pre-metallization surface treated contacts were the lowest achieved in this work. Interfacial oxide that may be present in the as-deposited contact due to ex-situ pre-metallization surface treatments (such as (NH$_4$)$_2$S and H$_2$O) is the significant factor in the determining the contact resistance of as-deposited Mo-based contacts to GeTe. Upon annealing, $R_c$ of Mo/Ti/Pt/Au (15/15/15/100 nm) contacts slightly increased with increasing annealing temperature, which might be attributed to the diffusion of Te and Ge into the Mo layer with annealing, although more study is warranted.
Chapter 6
Au Ohmic Contacts to GeTe

6.1 Introduction

In this chapter, Au Ohmic contacts to GeTe are discussed in terms of contact resistance ($R_c$), morphological changes and thermal stability. Au has a high work function (5.1 eV)\textsuperscript{47} comparable to Ni, which would provide a Schottky-Mott barrier height for Au/GeTe interface of -0.58 eV. Au is in thermodynamic equilibrium with GeTe and no reaction is anticipated\textsuperscript{48}. Moreover, an elemental contact is easier to fabricate from the thermodynamic point of view compared to an alloyed or layered contacts. However, one should keep in mind that the Au-Ge system has a low eutectic temperature of 361 °C\textsuperscript{49}.

6.2 Contact Resistance Results

6.2.1 Contact Resistance as a Function of Surface Treatment

Figure 6.1a (6.1b) shows measured $R_c$ ($\rho_c$) of 100 nm Au contacts to GeTe as a function of various pre-metallization surface preparation procedures. The various surface treatments barely changed the contact resistance $R_c$ ($\rho_c$) of the Au contacts. This behavior can be attributed to the low reactivity of Au with GeTe, Ge, and Te compared to Ni contacts, wherein the strong reactivity of Ni resulted in formation of different phases for different surface treatments that resulted in different $R_c$. The minimal fluctuation observed in $\rho_c$ can be attributed to sample-to-sample variation. These results differ greatly from the Ni- and Mo-based contacts, where $R_c$ ($\rho_c$) showed a strong dependence on surface treatments and the corresponding surface stoichiometries. Table 6.1 summarizes different surface preparation procedures for the as-deposited Au contacts to GeTe and their relevant extracted resistance values.
Figure 6.1: Dependence of (a) $R_c$ and (b) $\rho_c$ on surface preparation procedures prior to metallization of 100 nm Au contacts to GeTe.

Table 6.1: Summary of the extracted data from $I$-$V$ measurements for the as-deposited Au contacts as a function of different pre-metallization surface preparation procedures. (Those values were extracted using gap spacings $\leq 2$ µm. For more details, see Appendix D.)

<table>
<thead>
<tr>
<th>Surface treatment</th>
<th>$R_c$ ($\Omega$ mm)</th>
<th>$\rho_c$ ($\Omega$ cm$^2$)</th>
<th>$R_{sh}$ ($\Omega$ µm$^{-1}$)</th>
<th>$L_4$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar$^+$ plasma</td>
<td>0.007 ± 0.001</td>
<td>1.2 ± 0.4 × 10$^{-8}$</td>
<td>46.2 ± 0.5</td>
<td>0.15 ± 0.02</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.007 ± 0.001</td>
<td>1.2 ± 0.4 × 10$^{-8}$</td>
<td>43.0 ± 1.6</td>
<td>0.17 ± 0.03</td>
</tr>
<tr>
<td>(NH$_4$)$_2$S</td>
<td>0.007 ± 0.001</td>
<td>1.3 ± 0.4 × 10$^{-8}$</td>
<td>42.6 ± 1.6</td>
<td>0.17 ± 0.01</td>
</tr>
<tr>
<td>HCl</td>
<td>0.007 ± 0.001</td>
<td>1.2 ± 0.1 × 10$^{-8}$</td>
<td>44.5 ± 1.0</td>
<td>0.16 ± 0.01</td>
</tr>
</tbody>
</table>
6.2.2 Contact Resistance as a Function of Annealing

Annealing of Ar$^+$ plasma-treated Au contacts (100 nm) with and without 10 nm SiO$_2$ capping layer was examined. The SiO$_2$ capping layer was introduced to suppress the GeTe cracking phenomena and Te evaporation as discussed in Chapter 2. The effect of annealing was investigated at three different annealing temperatures (250, 300, and 350 $^\circ$C) for 30 min. $R_c$ ($\rho_c$) of the Au contacts increased slightly after annealing as shown in Figure 6.2a-b. The increase in the contact resistance upon annealing can be attributed to the slight microstructure changes in both the GeTe and Au metal layers upon annealing. The sheet resistance ($R_{sh}$) values extracted for all capped contacts were fairly constant after annealing, indicating that the $R_{sh}$ between the contacts did not change much with annealing. On the other hand, the $R_{sh}$ of the uncapped sample decreased, indicating that $R_{sh}$ between the contacts changed when the contacts were annealed at 350 $^\circ$C for 30 min without a capping layer. The results are summarized in Table 6.2.

![Figure 6.2: (a) $R_c$ and (b) $\rho_c$ of Ar$^+$ plasma-treated Au contacts to GeTe as a function of annealing temperature.](image-url)
Table 6.2: Summary of the extracted data from I-V measurements for the as-deposited Ar$^+$ plasma-treated Au contacts as a function of annealing. (Those values were extracted using gap spacings ≤ 2 µm. For more details see Appendix D.)

<table>
<thead>
<tr>
<th>Annealing Temperature</th>
<th>$R_c$ ($\Omega$.mm)</th>
<th>$\rho_c$ ($\Omega$.cm$^2$)</th>
<th>$R_{sh}$ ($\Omega$.\sqmu)</th>
<th>$L_t$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capped with 10 nm SiO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250 °C</td>
<td>0.009 ± 0.001</td>
<td>$2.0 \pm 0.6 \times 10^{-8}$</td>
<td>46.2 ± 1.7</td>
<td>0.21 ± 0.03</td>
</tr>
<tr>
<td>300 °C</td>
<td>0.009 ± 0.004</td>
<td>$2.6 \pm 2.4 \times 10^{-8}$</td>
<td>42.8 ± 4.8</td>
<td>0.23 ± 0.12</td>
</tr>
<tr>
<td>350 °C</td>
<td>0.013 ± 0.001</td>
<td>$3.6 \pm 0.8 \times 10^{-8}$</td>
<td>43.8 ± 1.7</td>
<td>0.29 ± 0.03</td>
</tr>
<tr>
<td>Uncapped</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>350 °C</td>
<td>0.012 ± 0.004</td>
<td>$3.1 \pm 0.7 \times 10^{-8}$</td>
<td>37.3 ± 0.8</td>
<td>0.28 ± 0.03</td>
</tr>
</tbody>
</table>

6.3 Morphological characterization

The Au contacts were inspected using scanning electron microscopy (SEM) before and after annealing to learn if significant changes of the morphology of the GeTe and Au surfaces occurred.

6.3.1 GeTe between the Contacts

The SEM images in Figure 6.3 show the effect of annealing temperature on GeTe microstructure between the contacts of SiO$_2$ capped Ar$^+$ plasma-treated Au contacts. The surface morphology reveals much more cracking as annealing temperature increases. The cracks in the GeTe film become deeper and wider compared to the shallow cracks on the as-deposited contacts. Crack propagation in the GeTe film impacts the measured $R_c$. 
Figure 6.3: SEM micrographs showing the changes in the GeTe microstructure as a function of annealing temperature.

6.3.2 Au Metallization Layer

Defects start evolving in the Au metallization layer and grow in size as annealing temperature increases as shown in Figure 6.4. Those defects have a rod-like structure with size depending strongly on the annealing temperature. It seems that those defects form due to sublimation of Te during annealing from the grain boundaries in the Au layer. Figure 6.5 show an energy dispersive spectroscopy (EDS) map of the Au surface after annealing at 350 °C for 30 min showing the rod-like defects in the Au metal layer.
Figure 6.4: SEM images of the Au film surface before and after annealing, showing defects formation in the Au layer upon annealing.

Figure 6.5: EDS map of the Au surface of the 350 °C annealed sample.
6.4 XTEM and EDS Characterization

In order to further elucidate the impact of annealing on Au contacts, TEM and EDS were used to investigate the morphological and chemical changes before and after annealing.

6.4.1 As-Deposited

A high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) image in Figure 6.6a shows the cross-section of as-deposited Ar⁺ plasma-treated Au contact with nominal deposited thickness of 100 nm with measured $R_c = 0.007 \pm 0.001 \ \Omega \cdot \text{mm}$. No reaction between Au and GeTe is observed.

Figure 6.6: (a) HAADF STEM image of as-deposited Ar⁺ plasma-treated Au (100 nm) contact. (b) SAED of the GeTe in the channel region. (c) SAED of the GeTe under the left contact.
The selected area electron diffraction (SAED) pattern in Figure 6.6b of the GeTe in the channel shows that the GeTe was polycrystalline with a preferred orientation. Figure 6.6c shows the SAED pattern of the GeTe under the contacts, which is polycrystalline with clearly defined textures that vary by location. The strong preferential orientation of the channel is lost under the contact.

Figures 6.7a and 6.7b show the HAADF STEM image and EDS map, respectively, of the as-deposited Au contact. EDS results show a sharp interface and suggest that no reaction between Au and GeTe occurred.

6.4.2 Annealed at 350 °C, 30 min

For the Ar⁺ plasma-treated GeTe, the (100 nm) Au contact annealed at 350 °C for 30 min with measured $R_c = 0.013 \pm 0.001 \, \Omega \cdot \text{mm}$ (Figure 6.8a). A representative HAADF STEM image of the cross-section shows no reaction after annealing. However, delamination of the GeTe from the Si₃Ni₄ layer was observed, which appears as dark contrast between the GeTe and Si₃Ni₄ layers. Also, voids formed in both the GeTe and Au films.
After annealing, the channel retained its polycrystalline state with preferred orientation. (Figure 6.8b). However, the SAED pattern of the GeTe under the contact metals, while still polycrystalline, appears to have experienced some change in texture (Figure 6.8c). The annealed sample shows more diffracted planes compared to the as-deposited contact. This suggests that annealing the Au contacts causes the GeTe under the contacts to become more randomly oriented, while effecting little change to the channel. In an attempt to measure the GeTe sheet resistance after annealing, a blanket Au/GeTe (100/110 nm) sample was annealed at the same conditions. Then TFA, a potassium iodide and iodine based gold etchant, was used in an attempt to selectively etch away the Au layer. However, TFA etched GeTe, too.

Figure 6.8: (a) HAADF STEM image of Au (100 nm) contact capped with 10 nm of SiO₂ and annealed at 350 °C for 30 min. (b) SAED of the GeTe in the channel region. (c) SAED of the GeTe under the contact.
Bright field XTEM image of the annealed Au contact in Figure 6.9 shows no reaction between the Au and GeTe. A sharp interface is maintained even after annealing at 350 °C for 30 min. Additionally, the HAADF STEM and EDS map in Figure 6.10 support the lack of reaction between Au and GeTe upon annealing.

Figure 6.9: Bright field XTEM of annealed Au contact.

Figure 6.10: (a) HAADF STEM image and (b) EDS map of Ar⁺ plasma-treated Au (100 nm) contact annealed at 350 °C for 30 min.
Figures 6.11a and 6.11b show the HAADF STEM image and EDS map, respectively, of a rod-like defect seen earlier in Figures 6.4 and 6.5 revealing outdiffusion of Te (Figure 6.11c) and a little bit of Ge (Figure 6.11d) through the defect. These defects might be the reason behind the slight increase in the contact resistance with annealing.

Figure 6.11: (a) HAADF STEM image, (b) EDS map of Ar\(^+\) plasma-treated Au (100 nm) annealed at 350 °C for 30 min capped with 10 nm of SiO\(_2\). Individual (c) Te and (d) Ge EDS elemental maps are shown.
6.5 I-V-T measurements

As discussed in Chapter 1, in the presence of a Schottky barrier there are three distinguishable current transport mechanisms: thermionic emission (TE), thermionic field emission (TFE), and field emission (FE). A specific contact resistance ($\rho_c$) dependence over a temperature range is essential in order to differentiate between current transport mechanisms. Au contacts (100 nm) treated with Ar$^+$ plasma contact resistance were measured at room temperature 300K and ~77K by immersing the sample in liquid N$_2$ during the measurement to gain insight on the current transport mechanism across the Au/GeTe interface. Figure 6.12 shows the $R_c$, $\rho_c$, and $R_{sh}$ as a function of measurement temperature, showing a very mild decrease in the contact resistance when the temperature is decreased. Furthermore, the sheet resistance of GeTe film decreased with decreasing temperature, but only a small amount. This result is consistent with the decrease in the resistivity of the GeTe films with decreasing temperature, as reported by Bahl et al.$^{21}$ The result suggests that the transport of the current at the Au/GeTe interface cannot be describe by thermionic emission (TE).

Figure 6.12: (a) $R_c$, (b) $\rho_c$, and (c) $R_{sh}$ of Ar$^+$ plasma-treated Au (100 nm) contact as a function of temperature
6.6 Au-Ge-Te Ternary Phase Diagram Calculation Results

The resultant Au-Ge-Te ternary phase diagram from our thermodynamic calculations are shown in Figures 6.14a and 6.13b without and with the inclusion of the \( \gamma \)-GeTe phase, respectively. The ternary phase diagram suggests that Au is in thermodynamic equilibrium with GeTe and no reaction between Au and GeTe is anticipated, consistent with ref. 48. It should be noted that the inclusion of the \( \gamma \)-GeTe phase did not affect the result.

![Ternary phase diagrams of the Au-Ge-Te system (a) without and (b) with the inclusion of the \( \gamma \)-GeTe phase in the calculation.](image)

6.7 Conclusions

The measured contact resistance values for (100 nm) Au contacts to GeTe were low compared to Ni-based contacts, but higher than that of the Mo-based contacts. No reaction of Au with GeTe occurred, consistent with our expectations from thermodynamics. A sharp interface was maintained even after annealing at 350 °C for 30 min. The contact resistance values slightly increased after annealing. The increase in the contact resistance after annealing is correlated with defects evolving in the Au metal layer and outdiffusion of Te through these defects.
Chapter 7
Conclusions and Future Work

7.1 Conclusions

In this thesis, the contact resistance of M/GeTe, where M = Ni, Mo, Au, was investigated by changing several factors, including metallization surface treatments, and annealing temperatures.

First, surfaces of polycrystalline α-GeTe films were studied using x-ray photoelectron spectroscopy (XPS) after different surface treatments, including UV-O₃, in-situ Ar⁺ ion etching, deionized water (DI water), ammonium sulfide (NH₄)₂S, and hydrochloric acid (HCl), in an effort to understand the effect of pre-metallization surface treatments on contact resistance of different metal/GeTe contacts. The Ge 2p₃/₂, Te 3d₅/₂, S 2p, and Cl 2p core level peaks were examined together with the C 1s and O 1s peaks. The results suggested that the combination of UV-O₃ and subsequent oxide removal procedures not only removes surface oxides but also alters the GeTe surface stoichiometry. Ar⁺ plasma, DI H₂O, and (NH₄)₂S preparations leave the GeTe surface richer in Ge compared to the HCl treatment, which leaves the surface Te-rich. (NH₄)₂S treatment also oxidizes Ge and consequently etches the GeTe film. Furthermore, the stability of surfaces treated with H₂O, HCl, or (NH₄)₂S when left in air was investigated. None of these treatments passivate the surface, and the surface was prone to quick oxidation again.

The trend in the as-deposited contact resistance (Rₛ) and specific contact resistance (ρₛ) values as a function of surface treatments demonstrated a dependence on the choice of the metal used. For Ni/Ti/Pt/Au (30/15/15/100 nm) contacts, all treatments resulted in the same Rₛ ≈ 0.014 Ω.mm (ρₛ ≈ 4 × 10⁻⁸ Ω.cm²) except for the HCl treatment, which showed more than two times higher Rₛ and one order of magnitude higher ρₛ. The cross-sectional transmission microscopy (XTEM) and energy dispersive spectroscopy (EDS) results of Ni/GeTe interface revealed two particularly significant findings: (1) the ability of Ni to displace the surface oxides at the interface, and (2) strong reactivity between Ni and GeTe at room temperature, forming different phases as a function of surface treatment. The high contact resistance of the HCl-treated samples is ascribed to the formation of a 5nm thick...
layer of Ni$_{1.29}$Te at the interface. In contrast, constant $R_c \approx 0.007$ $\Omega$.mm and $\rho_c \approx 1.2 \times 10^{-8}$ $\Omega$.cm$^2$ were found for Au (100 nm) contacts, regardless of the surface treatment used. This finding might be attributed to the low reactivity of Au with GeTe. Mo/Ti/Pt/Au (5/15/15/100 nm) contacts also have shown a strong dependence on the surface treatment prior to metallization. The Ar$^+$ plasma-treated Mo-based contacts yielded lower $R_c$ and $\rho_c$ values ($\sim 0.005$ $\Omega$.mm and $\sim 7.2 \times 10^{-9}$ $\Omega$.cm$^2$, respectively) than H$_2$O and (NH$_4$)$_2$S treatments. All three of these treatments result in a Ge-rich interface; however, Ar$^+$ plasma is the only treatment that results in an oxide-free interface. XTEM and EDS results revealed extremely limited if any reaction between Mo and GeTe at room temperature. For many samples studied in this work, the metal deposition process appears to have possibly induced changes in the crystallinity of the GeTe under the contacts, as observed by a series of selected area electron diffraction (SAED) patterns of the GeTe under and between the contacts.

Figures 7.1a and 7.1b show a comparison of $R_c$ and $\rho_c$ for different metallization schemes using Ar$^+$ plasma treatment. Mo-based contacts consistently showed the lowest $R_c$ and $\rho_c$ values, the Au contacts were slightly higher, followed by the Ni-based contacts. The higher values of Ni-based contacts compared to the Au and Mo can be attributed to reactions, whereas Au and Mo-based contacts exhibited little to no reaction at room temperature, either due to thermodynamic (Au) or kinetic (Mo) reasons.

Figure 7.1: (a) $R_c$ and (b) $\rho_c$ as a function of different metallization schemes using Ar$^+$ plasma treatment (as-deposited).
Upon annealing, Ni-based contacts degraded electrically and mechanically, leading to serious reliability problems. The contact resistance of Mo/Ti/Pt/Au (15/15/15/100 nm) contacts slightly increased with increasing annealing temperature, which might be attributed to relatively slow outdiffusion of Te and Ge into the Mo layer with annealing, but this possibility requires more thorough study. Additionally, the contact resistance of Au (100 nm) contacts also slightly increased after annealing, even though a sharp interface was maintained after annealing at 350 °C for 30 min. However, formation of rod-like defects was seen in the Au contacts, accompanied by outdiffusion of Te through these defects as the annealing temperature increase.

I-V-T measurements of as-deposited Ar$^+$ plasma-treated Au contacts (100 nm) suggested negligible thermionic emission (TE) across the Au/GeTe interface. In order to predict the dominant transport mechanism, the characteristic tunneling energy ($E_{00}$) and thermal energy ($kT$) were compared. The $E_{00}$ was calculated to be 0.029 eV using equation (1.10) assuming an intrinsic hole concentration of approximately $1 \times 10^{20}$ cm$^{-3}$, light hole effective mass$^{88}$ of 1.15$m_0$ and an optical dielectric constant$^{89}$ of 36$\varepsilon_0$. At room temperature ($kT = 0.025$eV), $E_{00} \approx kT$; however, at 77K, $E_{00} >> kT$, which suggests that field emission (FE) is the principal current transport mechanism at the metal/GeTe interface. Furthermore, the lack of temperature dependence for the specific contact resistance ($\rho_c$) of the Au/GeTe contacts suggests FE being the main current transport mechanism across the metal/GeTe interface. The $\rho_c$ was calculated for different Schottky barrier heights ($\phi_B = 0.01–0.25$ eV) assuming FE using equation (1.8) as given by Robinson$^{41}$. When comparing the experimental values with the calculated values, as in Figure 7.2, barrier heights of 0.11, 0.12, and 0.14 eV are extracted for as-deposited Ar$^+$ plasma-treated Mo, Au, and Ni-based contacts to GeTe, respectively. The higher calculated barrier height for Ni can be attributed to the reactivity of Ni with GeTe at room temperature forming an interfacial layer affecting the tunneling resistance, while Au and Mo do not react with GeTe at room temperature.
Figure 7.2: Theoretical specific contact resistance as a function of barrier heights for GeTe assuming that current transport is by FE. Experimental data from the as-deposited Ar$^+$ plasma-treated Au, Mo, and Ni contacts are plotted.

Another interesting question that comes to mind is how low the contact resistance of metal/GeTe contacts can be? Is it really possible that the specific contact resistance could become as low as shown in Figure 7.2 for a vanishing barrier height?

In a metal/semiconductor contact, the contact resistance can be attributed to three main contributions: barrier contact resistance ($R_{\text{barrier}}$), contamination contact resistance ($R_{\text{contamination}}$), and quantum contact resistance ($R_o$). The barrier contact resistance originates from the formation of barrier (field emission transport in GeTe case) at the metal/semiconductor interface; whereas the contamination resistance is attributed to existence of contaminant at the interface such as native oxides. The quantum contact resistance describes the contact resistance between an infinite contact and a thin channel
resistance describes the contact resistance between an infinite contact and a thin channel and is equal to 12.9 kΩ per conducting mode\textsuperscript{90}. For a degenerate semiconductor with isotropic single-band-minimum semiconductor, the fundamental contact resistivity can be approximated\textsuperscript{91},

\[
\frac{1}{\rho_c} = \left(\frac{q^2}{\hbar} \left(\frac{3}{8\pi}\right)^{2/3} p^{2/3}\right)
\]  

(7.1)

where \( q \) is the electron charge, \( \hbar \) is reduced Planck constant, and \( p \) is the semiconductor carrier concentration.

In metal/GeTe contacts, if we assume that \( R_{\text{barrier}}=0 \), \( R_c \) can be describe by the summation of the \( R_{\text{contamination}} \) and \( R_0 \). Considering a 110 nm thick GeTe layer with hole concentration of \( 1 \times 10^{20} \text{ cm}^{-3} \) and \( R_{\text{sh}}= 40 \Omega. \text{ cm}^{-1} \), a lower limit of \( R_0 \approx 0.003 \Omega. \text{ mm} \) (\( \rho_0 \approx 2.5 \times 10^{-9} \Omega. \text{ cm}^2 \)) is estimated. Again, it should be noted that this calculation is overly simplified by the assumption of parabolic energy dispersion in the valance band for GeTe (which is not the case). This \( \rho_0 \) corresponds to the same resisted predicted for transport by FE a Schottky barrier height of \( \approx 0.09 \text{ eV} \), below which the benefit to reducing the \( \phi_B \) becomes small, as shown in Figure 7.2.

All \( \rho_c \) reported in this work are still higher than this limit. If we consider the \( \text{Ar}^+ \) plasma treated Mo-based contacts, \( \rho_c \approx 7 \times 10^{-9} \Omega. \text{ cm}^2 \) was found from our experiments. This value is a little bit higher than the rough estimate for \( \rho_o \). Using DI H\textsubscript{2}O and (NH\textsubscript{4})\textsubscript{2}S treatments for the same metallization resulted in higher \( R_c \approx 0.007 \Omega. \text{ mm} \) (\( \rho_c \approx 1 \times 10^{-8} \Omega. \text{ cm}^2 \)) due to the existence of an oxide interfacial layer giving rise to an additional tunneling resistance.

\section*{7.2 Future Work}

The electrical and morphological behaviors of the contacts studied in this thesis suggest several areas of further work regarding the improvement of the Ohmic contacts to GeTe for GeTe-based RF switches.

GeTe crystallinity changes induced by metallization raise the question about how this change affects the sheet resistance of the GeTe under the contacts. If they are not the
extract as much fundamental information about the metal/semiconductor contact as we might like. This observation emphasizes the need for detailed and careful study of the impact of metallization on the crystallinity of GeTe using cross-sectional transmission electron microscopy (TEM), selected area electron diffraction (SAED), and Bragg-Brentano geometry X-ray diffraction (XRD).

Another interesting investigation would be the impact of the coexistence of a second phase (elemental Ge) in the α-GeTe films, which has been confirmed using XPS, XTEM, and EDS. In the elemental Ge regions, a small amount of Te could be dissolved, which is known to be a donor in Ge\textsuperscript{92}. A barrier might form between the n\textsuperscript{+}-Ge and p\textsuperscript{++}-GeTe acting like small p-n junctions in the GeTe film. How would this affect the current transport in the GeTe and across the metal/GeTe interface?

Since Ar\textsuperscript{+} plasma-treated Mo-based contacts yielded the lowest contact resistance, but might have reacted at high temperatures, Mo\textsubscript{5}Ge\textsubscript{3} contacts to GeTe might be a promising candidate to achieve thermally stable contacts with extremely low resistance. We note especially that the Mo-based contact was made to a Ge-rich surface. From our thermodynamic calculation, Mo\textsubscript{5}Ge\textsubscript{3} may be in thermodynamic equilibrium with GeTe at room temperature. This contact should therefore be tested.
References


S.G. Karbanov, V.P.Zlomanov, and A.V. Novoselova, Doklady Chemistry 182, 862 (1968).


Appendix A

XPS Deconvolutions of Te 3d_{3/2} XPS Core Peak as a Function of Different Surface Treatments

Figure A.1: Representative deconvolutions of Te 3d_{3/2} XPS core peak is shown after (a) degreasing, (b) 10 min of UV-O_3, (c) 10 min of UV-O_3 followed by 5 min Ar^+ plasma etching, (d) 10 min of UV-O_3 followed by DI H_2O for 5 min, (e) 10 min of UV-O_3 followed by (10:1) H_2O:HCl for 120 s, and (f) 10 min of UV-O_3 followed by (100:1) H_2O:(NH_4)_2S for 30 s.
## Appendix B

### Ni-based Ohmic Contacts Detailed Results

*Table B.1: Summary of the extracted data from I-V measurements for the as-deposited Ni/Ti/Pt/Au (30/15/15/100 nm) contacts as a function of surface treatments extracted from gap spacings between 0.6 to 20 µm.*

<table>
<thead>
<tr>
<th>Surface treatment</th>
<th>$R_c$ ($Ω\cdot mm$)</th>
<th>$ρ_c$ ($Ω\cdot cm^2$)</th>
<th>$R_{sh}$ ($Ω\cdot 1^{-1}$)</th>
<th>$L_t$ ($µm$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar$^+$ plasma</td>
<td>0.016 ± 0.001</td>
<td>6.36 ± 0.65 × $10^{-8}$</td>
<td>40.03 ± 0.8</td>
<td>0.40 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>0.016 ± 0.001</td>
<td>6.59 ± 0.90 × $10^{-8}$</td>
<td>40.78 ± 0.33</td>
<td>0.40 ± 0.03</td>
</tr>
<tr>
<td>Average</td>
<td>0.016 ± 0.000</td>
<td>6.47 ± 0.16 × $10^{-8}$</td>
<td>40.40 ± 0.53</td>
<td>0.40 ± 0.00</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.018 ± 0.002</td>
<td>7.93 ± 1.57 × $10^{-8}$</td>
<td>42.88 ± 0.33</td>
<td>0.43 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>0.014 ± 0.002</td>
<td>4.76 ± 1.40 × $10^{-8}$</td>
<td>44.81 ± 0.32</td>
<td>0.32 ± 0.18</td>
</tr>
<tr>
<td>Average</td>
<td>0.016 ± 0.003</td>
<td>6.34 ± 2.24 × $10^{-8}$</td>
<td>43.84 ± 1.36</td>
<td>0.37 ± 0.08</td>
</tr>
<tr>
<td>(NH$_4$)$_2$S</td>
<td>0.018 ± 0.002</td>
<td>7.12 ± 2.47 × $10^{-8}$</td>
<td>44.98 ± 2.40</td>
<td>0.40 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>0.016 ± 0.001</td>
<td>6.02 ± 0.71 × $10^{-8}$</td>
<td>45.02 ± 0.65</td>
<td>0.37 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>0.015 ± 0.001</td>
<td>5.08 ± 0.81 × $10^{-8}$</td>
<td>43.55 ± 0.49</td>
<td>0.34 ± 0.03</td>
</tr>
<tr>
<td>Average</td>
<td>0.016 ± 0.001</td>
<td>6.07 ± 1.02 × $10^{-8}$</td>
<td>44.52 ± 0.84</td>
<td>0.37 ± 0.03</td>
</tr>
<tr>
<td>HCl</td>
<td>0.038 ± 0.007</td>
<td>3.47 ± 1.37 × $10^{-7}$</td>
<td>43.33 ± 0.30</td>
<td>0.88 ± 0.17</td>
</tr>
<tr>
<td></td>
<td>0.035 ± 0.002</td>
<td>2.82 ± 0.33 × $10^{-7}$</td>
<td>43.65 ± 1.71</td>
<td>0.80 ± 0.06</td>
</tr>
<tr>
<td>Average</td>
<td>0.036 ± 0.002</td>
<td>3.14 ± 0.46 × $10^{-7}$</td>
<td>43.49 ± 0.27</td>
<td>0.84 ± 0.06</td>
</tr>
</tbody>
</table>
Table B.2: Summary of the extracted data from I-V measurements for the as-deposited Ni/Ti/Pt/Au (30/15/15/100 nm) contacts as a function of surface treatments extracted from gap spacings between 0.6 to 2 µm.

<table>
<thead>
<tr>
<th>Surface treatment</th>
<th>$R_s$ (Ω.mm)</th>
<th>$\rho_s$ (Ω.cm$^2$)</th>
<th>$R_{sh}$ (Ω.□$^{-1}$)</th>
<th>$L_t$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar$^+$ plasma</td>
<td>0.015 ± 0.003</td>
<td>5.55 ± 1.36 × 10$^{-8}$</td>
<td>43.61 ± 3.46</td>
<td>0.35 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>0.013 ± 0.002</td>
<td>3.58 ± 1.59 × 10$^{-8}$</td>
<td>45.99 ± 6.13</td>
<td>0.28 ± 0.08</td>
</tr>
<tr>
<td>Average</td>
<td><strong>0.014 ± 0.001</strong></td>
<td><strong>4.56 ± 1.39 × 10$^{-8}$</strong></td>
<td><strong>44.80 ± 1.68</strong></td>
<td><strong>0.31 ± 0.05</strong></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.017 ± 0.003</td>
<td>7.26 ± 3.09 × 10$^{-8}$</td>
<td>44.27 ± 5.85</td>
<td>0.40 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>0.010 ± 0.003</td>
<td>2.32 ± 1.20 × 10$^{-8}$</td>
<td>50.28 ± 2.33</td>
<td>0.21 ± 0.23</td>
</tr>
<tr>
<td>Average</td>
<td><strong>0.013 ± 0.005</strong></td>
<td><strong>4.79 ± 3.49 × 10$^{-8}$</strong></td>
<td><strong>47.27 ± 4.25</strong></td>
<td><strong>0.30 ± 0.13</strong></td>
</tr>
<tr>
<td>(NH$_4$)$_2$S</td>
<td>0.014 ± 0.006</td>
<td>4.63 ± 3.21 × 10$^{-8}$</td>
<td>45.16 ± 1.97</td>
<td>0.29 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>0.016 ± 0.001</td>
<td>6.13 ± 1.22 × 10$^{-8}$</td>
<td>45.16 ± 1.97</td>
<td>0.37 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>0.012 ± 0.001</td>
<td>3.01 ± 0.55 × 10$^{-8}$</td>
<td>48.66 ± 1.90</td>
<td>0.25 ± 0.03</td>
</tr>
<tr>
<td>Average</td>
<td><strong>0.014 ± 0.002</strong></td>
<td><strong>4.59 ± 1.56 × 10$^{-8}$</strong></td>
<td><strong>48.19 ± 2.83</strong></td>
<td><strong>0.30 ± 0.06</strong></td>
</tr>
<tr>
<td>HCl</td>
<td>0.036 ± 0.007</td>
<td>2.91 ± 1.11 × 10$^{-7}$</td>
<td>46.52 ± 5.5</td>
<td>0.78 ± 0.19</td>
</tr>
<tr>
<td></td>
<td>0.032 ± 0.002</td>
<td>2.18 ± 0.44 × 10$^{-7}$</td>
<td>48.27 ± 5.19</td>
<td>0.67 ± 0.10</td>
</tr>
<tr>
<td>Average</td>
<td><strong>0.034 ± 0.003</strong></td>
<td><strong>2.54 ± 0.52 × 10$^{-7}$</strong></td>
<td><strong>47.39 ± 2.83</strong></td>
<td><strong>0.72 ± 0.08</strong></td>
</tr>
</tbody>
</table>
Table B.3: Summary of the extracted data from I-V measurements for the annealed Ni/Ti/Pt/Au (30/15/15/100 nm) contacts as a function of surface treatments and annealing temperature extracted from gap spacings between 0.6 to 20 µm.

<table>
<thead>
<tr>
<th>Surface treatment</th>
<th>Temperature (°C)</th>
<th>$R_c$ (Ω.mm)</th>
<th>$\rho_c$ (Ω.cm$^2$)</th>
<th>$R_{sh}$ (Ω.□$^{-1}$)</th>
<th>$L_t$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH$_4$)$_2$S</td>
<td>250</td>
<td>0.154 ± 0.052</td>
<td>7.4 ± 4.3 × 10$^{-6}$</td>
<td>39.1 ± 10.3</td>
<td>4.33 ± 1.99</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>0.019 ± 0.004</td>
<td>1.3 ± 0.5 × 10$^{-8}$</td>
<td>29.5 ± 1.3</td>
<td>0.64 ± 0.13</td>
</tr>
<tr>
<td>HCl</td>
<td>350</td>
<td>0.021 ± 0.002</td>
<td>1.05 ± 0.2 × 10$^{-7}$</td>
<td>41.4 ± 2.56</td>
<td>0.50 ± 0.06</td>
</tr>
</tbody>
</table>

Table B.4: Summary of the extracted data from I-V measurements for the annealed Ni/Ti/Pt/Au (30/15/15/100 nm) contacts as a function of surface treatments and annealing temperature extracted from gap spacings between 0.6 to 2 µm.

<table>
<thead>
<tr>
<th>Surface treatment</th>
<th>Temperature (°C)</th>
<th>$R_c$ (Ω.mm)</th>
<th>$\rho_c$ (Ω.cm$^2$)</th>
<th>$R_{sh}$ (Ω.□$^{-1}$)</th>
<th>$L_t$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH$_4$)$_2$S</td>
<td>350</td>
<td>0.017 ± 0.001</td>
<td>9.6 ± 5.7 × 10$^{-8}$</td>
<td>32.5 ± 0.6</td>
<td>0.53 ± 0.19</td>
</tr>
<tr>
<td>HCl</td>
<td>350</td>
<td>0.013 ± 0.002</td>
<td>3.2 ± 1.5 × 10$^{-8}$</td>
<td>53.1 ± 5.5</td>
<td>0.24 ± 0.07</td>
</tr>
</tbody>
</table>
Appendix C
Mo-based Ohmic Contacts Detailed Results

*Table C.1:* Summary of the extracted data from I-V measurements for the as-deposited Mo-based contacts as a function of surface treatments, metal stacks, and metal thicknesses extracted from gap spacings between 0.6 to 20 µm.

| Metallization          | Surface treatment | $R_c$ (Ω.mm) | $ho_c$ (Ω.cm$^2$) | $R_{sh}$ (Ω. □$^{-1}$) | $L_t$ (µm) |
|------------------------|-------------------|--------------|---------------------|--------------------------|------------|
| Mo/Ti/Pt/Au (15/15/15/100 nm) | Ar$^+$ plasma    | 0.005 ± 0.001 | 4.9 ± 1.1 × 10$^9$ | 44.2 ± 0.2              | 0.11 ± 0.01|
|                        |                   | 0.006 ± 0.001 | 7.2 ± 2.5 × 10$^9$ | 42.7 ± 0.4              | 0.13 ± 0.02|
|                        | Average           | **0.005 ± 0.001** | **6.1 ± 1.6 × 10$^9$** | **43.5 ± 1.1** | **0.12 ± 0.01** |
| Mo/Ti/Pt/Au (5/15/15/100 nm) | Ar$^+$ plasma    | 0.006 ± 0.001 | 7.9 ± 0.8 × 10$^9$ | 42.3 ± 0.6              | 0.14 ± 0.01|
|                        | H$_2$O            | 0.008 ± 0.001 | 1.4 ± 0.2 × 10$^8$ | 44.3 ± 0.1              | 0.18 ± 0.01|
|                        | (NH$_4$)$_2$S     | 0.009 ± 0.001 | 2.0 ± 0.3 × 10$^8$ | 43.4 ± 0.3              | 0.21 ± 0.02|
| Mo/Au (35/100 nm)      | H$_2$O            | 0.009 ± 0.001 | 1.9 ± 0.4 × 10$^8$ | 40.8 ± 1.7              | 0.22 ± 0.03|
|                        | (NH$_4$)$_2$S     | 0.008 ± 0.001 | 1.4 ± 0.4 × 10$^8$ | 41.1 ± 0.9              | 0.18 ± 0.03|
Table C.2: Summary of the extracted data from I-V measurements for the as-deposited Mo-based contacts as a function of surface treatments, metal stacks, and metal thicknesses extracted from gap spacings between 0.6 to 2 µm.

<table>
<thead>
<tr>
<th>Metallization</th>
<th>Surface treatment</th>
<th>$R_c$</th>
<th>$\rho_c$</th>
<th>$R_{sh}$</th>
<th>$L_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Ω.mm)</td>
<td>(Ω.cm$^2$)</td>
<td>(Ω.□$^{-1}$)</td>
<td>(µm)</td>
</tr>
<tr>
<td>Mo/Ti/Pt/Au (5/15/15/100 nm)</td>
<td>Ar$^+$ plasma</td>
<td>0.005 ± 0.002</td>
<td>7.7 ± 4.6×10$^{-9}$</td>
<td>43.2 ± 2.2</td>
<td>0.13 ± 0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.006 ± 0.002</td>
<td>6.7 ± 7.1×10$^{-9}$</td>
<td>43.9 ± 3.1</td>
<td>0.11 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>0.005 ± 0.001</td>
<td>7.2 ± 0.7×10$^{-9}$</td>
<td>43.5 ± 0.5</td>
<td>0.12 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Ar$^+$ plasma</td>
<td>0.004 ± 0.001</td>
<td>2.9 ± 1.3×10$^{-9}$</td>
<td>44.6 ± 0.8</td>
<td>0.08 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>H$_2$O</td>
<td>0.008 ± 0.001</td>
<td>1.3 ± 0.3×10$^{-8}$</td>
<td>45.7 ± 2.4</td>
<td>0.17 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>(NH$_4$)$_2$S</td>
<td>0.008 ± 0.001</td>
<td>1.6 ± 0.2×10$^{-8}$</td>
<td>46.2 ± 3.4</td>
<td>0.19 ± 0.02</td>
</tr>
<tr>
<td>Mo/Au (35/100 nm)</td>
<td>H$_2$O</td>
<td>0.008 ± 0.001</td>
<td>1.7 ± 0.6×10$^{-8}$</td>
<td>41.4 ± 2.7</td>
<td>0.20 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>(NH$_4$)$_2$S</td>
<td>0.007 ± 0.003</td>
<td>1.4 ± 1.4×10$^{-8}$</td>
<td>43.8 ± 5.2</td>
<td>0.16 ± 0.09</td>
</tr>
</tbody>
</table>
Table C.3: Summary of the extracted data from I-V measurements for the annealed Mo/Ti/Pt/Au (15/15/15/100 nm) contacts with and without 10 nm SiO$_2$ capping layer as a function of annealing temperature (250, 300, 350°C) extracted from gap spacings between 0.6 to 20 µm.

<table>
<thead>
<tr>
<th>Annealing Temperature</th>
<th>$R_c$ ($\Omega \cdot \text{mm}$)</th>
<th>$\rho_c$ ($\Omega \cdot \text{cm}^2$)</th>
<th>$R_{sh}$ ($\Omega \cdot \text{cm}^{-1}$)</th>
<th>$L_t$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capped with 10 nm SiO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250 °C</td>
<td>0.016 ± 0.003</td>
<td>8.4 ± 3.4 × 10$^{-8}$</td>
<td>30.5 ± 2.5</td>
<td>0.52 ± 0.13</td>
</tr>
<tr>
<td>300 °C</td>
<td>0.017 ± 0.002</td>
<td>9.2 ± 1.9 × 10$^{-8}$</td>
<td>30.7 ± 1.5</td>
<td>0.55 ± 0.07</td>
</tr>
<tr>
<td>350 °C</td>
<td>0.012 ± 0.001</td>
<td>4.3 ± 1.0 × 10$^{-8}$</td>
<td>31.7 ± 0.2</td>
<td>0.37 ± 0.05</td>
</tr>
<tr>
<td>Uncapped</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250 °C</td>
<td>0.010 ± 0.001</td>
<td>3.1 ± 0.5 × 10$^{-8}$</td>
<td>36.8 ± 0.7</td>
<td>0.29 ± 0.02</td>
</tr>
<tr>
<td>300 °C</td>
<td>0.012 ± 0.001</td>
<td>4.1 ± 0.4 × 10$^{-8}$</td>
<td>35.4 ± 0.6</td>
<td>0.34 ± 0.02</td>
</tr>
<tr>
<td>350 °C</td>
<td>0.011 ± 0.001</td>
<td>3.5 ± 0.6 × 10$^{-8}$</td>
<td>36.8 ± 0.7</td>
<td>0.31 ± 0.03</td>
</tr>
</tbody>
</table>

Table C.4: Summary of the extracted data from I-V measurements for the annealed Mo/Ti/Pt/Au (15/15/15/100 nm) contacts with and without 10 nm SiO$_2$ capping layer as a function of annealing temperature (250, 300, 350°C) extracted from gap spacings between 0.6 to 2 µm.

<table>
<thead>
<tr>
<th>Annealing Temperature</th>
<th>$R_c$ ($\Omega \cdot \text{mm}$)</th>
<th>$\rho_c$ ($\Omega \cdot \text{cm}^2$)</th>
<th>$R_{sh}$ ($\Omega \cdot \text{cm}^{-1}$)</th>
<th>$L_t$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capped with 10 nm SiO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250 °C</td>
<td>0.009 ± 0.002</td>
<td>2.2 ± 1.0 × 10$^{-8}$</td>
<td>39.1 ± 2.9</td>
<td>0.23 ± 0.06</td>
</tr>
<tr>
<td>300 °C</td>
<td>0.007 ± 0.001</td>
<td>1.3 ± 0.4 × 10$^{-8}$</td>
<td>42.0 ± 2.7</td>
<td>0.17 ± 0.04</td>
</tr>
<tr>
<td>350 °C</td>
<td>0.007 ± 0.002</td>
<td>1.7 ± 0.9 × 10$^{-8}$</td>
<td>36.4 ± 1.1</td>
<td>0.21 ± 0.07</td>
</tr>
<tr>
<td>Uncapped</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250 °C</td>
<td>0.007 ± 0.002</td>
<td>1.3 ± 0.4 × 10$^{-8}$</td>
<td>41.0 ± 0.4</td>
<td>0.18 ± 0.03</td>
</tr>
<tr>
<td>300 °C</td>
<td>0.008 ± 0.001</td>
<td>1.7 ± 0.2 × 10$^{-8}$</td>
<td>39.9 ± 0.7</td>
<td>0.21 ± 0.02</td>
</tr>
<tr>
<td>350 °C</td>
<td>0.009 ± 0.001</td>
<td>2.0 ± 0.4 × 10$^{-8}$</td>
<td>40.1 ± 0.8</td>
<td>0.23 ± 0.02</td>
</tr>
</tbody>
</table>
Appendix D

Au Ohmic Contacts Detailed Results

Table D.1: Summary of the extracted data from $I$-$V$ measurements for the as-deposited Au (100 nm) contacts as a function of surface treatments extracted from gap spacings between 0.6 to 20 µm.

<table>
<thead>
<tr>
<th>Surface treatment</th>
<th>$R_c$ (Ω.mm)</th>
<th>$\rho_c$ (Ω.cm$^2$)</th>
<th>$R_{sh}$ (Ω.□$^{-1}$)</th>
<th>$L_t$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar$^+$ plasma</td>
<td>0.010 ± 0.001</td>
<td>2.4 ± 0.4 × 10$^{-8}$</td>
<td>43.0 ± 0.7</td>
<td>0.24 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>0.007 ± 0.001</td>
<td>1.1 ± 0.1 × 10$^{-8}$</td>
<td>44.6 ± 0.4</td>
<td>0.16 ± 0.01</td>
</tr>
<tr>
<td>Average</td>
<td>0.008 ± 0.002</td>
<td>1.7 ± 0.9 × 10$^{-8}$</td>
<td>43.8 ± 1.1</td>
<td>0.20 ± 0.06</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.008 ± 0.001</td>
<td>1.5 ± 0.1 × 10$^{-8}$</td>
<td>41.5 ± 0.1</td>
<td>0.19 ± 0.01</td>
</tr>
<tr>
<td>(NH$_4$)$_2$S</td>
<td>0.007 ± 0.001</td>
<td>1.3 ± 0.2 × 10$^{-8}$</td>
<td>40.4 ± 0.3</td>
<td>0.18 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>0.008 ± 0.001</td>
<td>1.6 ± 0.2 × 10$^{-8}$</td>
<td>42.6 ± 0.4</td>
<td>0.19 ± 0.02</td>
</tr>
<tr>
<td>Average</td>
<td>0.007 ± 0.001</td>
<td>1.4 ± 0.2 × 10$^{-8}$</td>
<td>41.5 ± 1.5</td>
<td>0.18 ± 0.01</td>
</tr>
<tr>
<td>HCl</td>
<td>0.009 ± 0.001</td>
<td>1.7 ± 0.1 × 10$^{-8}$</td>
<td>42.3 ± 0.1</td>
<td>0.20 ± 0.01</td>
</tr>
</tbody>
</table>
Table D.2: Summary of the extracted data from I-V measurements for the as-deposited Au (100 nm) contacts as a function of surface treatments extracted from gap spacings between 0.6 to 2 µm.

<table>
<thead>
<tr>
<th>Surface treatment</th>
<th>( R_c ) (Ω.mm)</th>
<th>( \rho_c ) (Ω.cm(^2))</th>
<th>( R_{sh} ) (Ω.□(^{-1}))</th>
<th>( L_t ) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar(^+) plasma</td>
<td>0.008 ± 0.003</td>
<td>1.5 ± 0.9 \times 10^{-8}</td>
<td>46.6 ± 3.6</td>
<td>0.17 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>0.006 ± 0.001</td>
<td>9.2 ± 2.5 \times 10^{-9}</td>
<td>45.9 ± 1.7</td>
<td>0.14 ± 0.02</td>
</tr>
<tr>
<td>Average</td>
<td>0.007 ± 0.001</td>
<td>1.2 ± 0.4 \times 10^{-8}</td>
<td>46.2 ± 0.5</td>
<td>0.15 ± 0.02</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>0.007 ± 0.001</td>
<td>1.2 ± 0.4 \times 10^{-8}</td>
<td>43.0 ± 1.6</td>
<td>0.17 ± 0.03</td>
</tr>
<tr>
<td>( \text{(NH}_4\text{)}_2\text{S} )</td>
<td>0.007 ± 0.001</td>
<td>1.0 ± 0.2 \times 10^{-8}</td>
<td>41.5 ± 0.8</td>
<td>0.16 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>0.008 ± 0.002</td>
<td>1.6 ± 1.1 \times 10^{-8}</td>
<td>43.8 ± 2.9</td>
<td>0.18 ± 0.07</td>
</tr>
<tr>
<td>Average</td>
<td>0.007 ± 0.001</td>
<td>1.3 ± 0.4 \times 10^{-8}</td>
<td>42.6 ± 1.6</td>
<td>0.17 ± 0.01</td>
</tr>
<tr>
<td>HCl</td>
<td>0.007 ± 0.001</td>
<td>1.2 ± 0.1 \times 10^{-8}</td>
<td>44.5 ± 1.0</td>
<td>0.16 ± 0.01</td>
</tr>
</tbody>
</table>

Table D.3: Summary of the extracted data from I-V measurements for the annealed Ar\(^+\) plasma-treated Au (100 nm) contacts as a function of annealing temperature extracted from gap spacings between 0.6 to 20 µm.

<table>
<thead>
<tr>
<th>Annealing Temperature</th>
<th>( R_c ) (Ω.mm)</th>
<th>( \rho_c ) (Ω.cm(^2))</th>
<th>( R_{sh} ) (Ω.□(^{-1}))</th>
<th>( L_t ) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capped with 10 nm SiO(_2)</td>
<td>250 °C</td>
<td>0.014 ± 0.002</td>
<td>5.0 ± 2.2 \times 10^{-8}</td>
<td>40.3 ± 3.3</td>
</tr>
<tr>
<td></td>
<td>300 °C</td>
<td>0.019 ± 0.001</td>
<td>1.2 ± 0.1 \times 10^{-7}</td>
<td>30.8 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>350 °C</td>
<td>0.021 ± 0.001</td>
<td>1.4 ± 0.1 \times 10^{-7}</td>
<td>33.1 ± 0.9</td>
</tr>
<tr>
<td>Uncapped</td>
<td>350 °C</td>
<td>0.015 ± 0.001</td>
<td>8.0 ± 1.5 \times 10^{-8}</td>
<td>30.3 ± 0.16</td>
</tr>
</tbody>
</table>
Table D.4: Summary of the extracted data from I-V measurements for the annealed Ar⁺ plasma-treated Au (100 nm) contacts as a function of annealing temperature extracted from gap spacings between 0.6 to 2 µm.

<table>
<thead>
<tr>
<th>Annealing Temperature</th>
<th>( R_c ) (Ω.mm)</th>
<th>( \rho_c ) (Ω.cm²)</th>
<th>( R_{sh} ) (Ω.□⁻¹)</th>
<th>( L_t ) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capped with 10 nm SiO₂</td>
<td>250 °C</td>
<td>0.009 ± 0.001</td>
<td>2.0 ± 0.6× 10⁻⁸</td>
<td>46.2 ± 1.7</td>
</tr>
<tr>
<td></td>
<td>300 °C</td>
<td>0.009 ± 0.004</td>
<td>2.6 ± 2.4× 10⁻⁸</td>
<td>42.8 ± 4.8</td>
</tr>
<tr>
<td></td>
<td>350 °C</td>
<td>0.013 ± 0.001</td>
<td>3.6 ± 0.8× 10⁻⁸</td>
<td>43.8 ± 1.7</td>
</tr>
<tr>
<td>Uncapped</td>
<td>350 °C</td>
<td>0.012 ± 0.004</td>
<td>3.1 ± 0.7× 10⁻⁸</td>
<td>37.3 ± 0.8</td>
</tr>
</tbody>
</table>
Vita

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EDUCATION

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