The Pennsylvania State University
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A MATERIALS APPROACH TO RESONANT MICROWAVE MICROPLASMA
GENERATORS

A Dissertation in
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by

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ABSTRACT

With the advent of microplasmas, what was once considered impossible, the generation of stable, high-density, non-equilibrium plasmas, was demonstrated in the lab. Such microplasmas have since found applications in diverse fields including nanomaterial synthesis, medicine, and metamaterials. One promising route to microplasma generation is through the use of microwaves. Microwave microplasmas, in particular, offer the benefit of low-sputtering damage and the potential for plasma breakdown occurring at voltages lower than predicted by Paschen’s Law. Such advantages over DC and lower frequency microplasma generation can extend the longevity of microplasma generators and improve consistency in operation. An additional advantage is the possibility for remote microplasma generation using microwaves, which can allow, for instance, wirelessly-operable plasma-reconfigurable metamaterials. In this dissertation, the materials aspects of resonant microwave microplasma generation are explored. A proof-of-concept for a new microplasma generator, the all-dielectric, microwave, microplasma generator is introduced. One main advantage of such a device over conventional resonators is the absence of reflective metal components — a feature that allows new possibilities for future plasma metamaterial designs. This work is followed by materials studies of split-ring resonator (SRR) microplasma generators. It is found that Q-factor and surface chemistry can play a large role in the performance of these devices. Studies of SRRs for plasma generation are continued with new manufacturing techniques including ns- and fs- laser ablation. The manufacturing technique is found to influence both Q-factor and breakdown performance independently — combined, these factors contribute to an order of magnitude difference in power required for plasma generation. Relatedly, microstructural and chemical analysis in addition to plasma breakdown voltage distributions give evidence that field emission is contributing seed electrons for breakdown at gap sizes up to approximately 40 µm.
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Chapter 1

Background and Overview

Technological plasmas have played a large role in materials processing and have been and continue to be the key to producing the small transistors that are the backbone of information technology. Perhaps more interestingly, plasmas are continuing to be useful in new applications in broad fields including energy, medicine, and defense. A type of plasma that is the driving force behind many new innovations is the microplasma. A plasma can be considered a microplasma if one of its dimensions is in the range of 1 µm to 1 mm. Microplasmas have the ability to remain in a stable, non-equilibrium state at atmospheric pressure. This means that new technologies can begin to benefit from the advantages of atmospheric-pressure plasmas such as high electron density and the lack of need for vacuum equipment, while potentially avoiding damage that is associated with unstable and/or thermal plasmas. Miniaturizing the plasmas has other benefits too, such as the ability to control plasma properties locally, the potential for better homogeneity over large areas, and the possibility of low power atmospheric pressure breakdown.

Coincidentally, in the early 2000s, around the same time scientists convened for the first conference dedicated to microplasma research, metamaterials arose as a new research paradigm in electromagnetics and materials. The definition for an electromagnetic metamaterial is broad, but in general, metamaterials consist of subwavelength, engineered structures that allow for tailored macroscopic electromagnetic properties — properties such as negative permittivity and permeability, which are difficult to achieve using natural materials. It took about a decade for these two technologies to merge and the concept of the plasma metamaterial to arise. Microplasmas are an interesting candidate for metamaterial components — their electromagnetic properties can be changed dynamically, which may allow reconfigurable metamaterials operating
in frequencies ranging from microwave to THz. In addition, they may be generated in different shapes for different metamaterial responses, they can natively offer negative permittivity, and they can be turned on and off with potentially ns response times. Figure 1-1 shows an array of microwave split-ring resonators (SRRs), a common component in metamaterials, generating microplasmas. The location of plasmas can be chosen by exciting the array with the resonant frequency of specific SRRs [1]. Work on such arrays is currently being explored in an attempt to produce a double negative material that utilizes both SRRs and plasmas [2, 3]. However, in the arrays shown in Fig. 1-1, about 1 W per resonator is required to generate plasma [1]. In addition, some of the resonators appear to no longer be functioning, and discoloring near the plasma generating gap is present on these resonators. The high-power requirements and damage on the resonators suggested that pathways be sought such that plasma generation power and damage could be reduced.

Figure 1-1: Arrays of split-ring resonators which are remotely excited to generate plasmas at (a) 2.1 GHz and (b) 2.45 GHz. Source: P.K. Singh, J. Hopwood, and S. Sonkusale, Scientific Reports 4, 1 (2014).
Despite the importance of plasmas to materials science, when it comes to microwave microplasmas the importance of materials science to microplasma generation has largely not been considered. A materials-focused approach, then, appears to be one potential pathway for reducing power and improving reliability of microplasma generation. The first direction pursued herein was to replace the SRR entirely. The electric field generated by the SRR is, in part, governed by its Q-factor, which is the ratio of energy stored per cycle in the resonator to the power lost by the resonator. Split-ring resonators in general have relatively poor Q-factors when compared to dielectric resonators because dielectric resonators do not suffer from conduction current losses. Chapter 2 of this dissertation explores plasma generation using a split dielectric resonator. A proof-of-concept for such a device, the first of its kind, was demonstrated. Around the same time, our collaborators demonstrated another variant of such a device by generating plasma between two dielectric resonators. With these all-dielectric platforms for plasma generation in place, new materials-related questions surfaced. Can microwave microplasma generation power be influenced by factors such as work function, surface morphology, and surface chemistry? With these questions in mind, it became evident that dielectric resonators would likely not be the best candidate for further study. Unlike SRRs, a precise understanding of the power required to generate plasmas was not as easily accessible using dielectric resonators. Dielectric resonators require remote excitation or relatively complex coupling schemes, whereas SRRs can be designed with a direct, easily-measured power input.

Chapter 3 explores the materials aspects of microplasma generation using screen-printed, microwave split-ring resonators at low pressure in Ar. The main contributions of the work discussed in this chapter is to show that Q-factor, when properly measured, was the main determinant of plasma breakdown performance in split-ring resonators with near-identical geometry and gap sizes of ~100 µm. A corollary of this result is that work function and surface morphology, within the limited parameters explored, were contributing little to plasma
breakdown performance. This suggests that field emission of electrons and electron losses due to porosity were likely not contributing to breakdown. However, another important aspect of this work was to explore the effects of film formation on plasma breakdown power. In particular, the formation of a film on an Ag SRR caused as much as a 20% increase in the power required for plasma generation. Such a detrimental film builds up quickly and therefore likely represents the steady-state performance of such a device. On the contrary, as discussed in Chapter 5, with an intentionally deposited film such as alumina, the breakdown power could be reduced by up to 30% while the SRR also gained protection from the film. Therefore, with the limited materials explored, up to a 50% reduction in power could be achieved. Unfortunately, these benefits were seen to decrease significantly as pressure was increased. This suggested that new approaches would need to be taken to improve performance at atmospheric pressure.

Chapter 4 primarily explores atmospheric pressure breakdown in Ag and Au SRRs fabricated using a variety of techniques. Plasma breakdown was found to be much different at atmospheric pressure than at the low-to-moderate pressures explored previously. Primarily, breakdown became much less predictable. Another important finding of this study is that fabrication method can play a large role in plasma breakdown performance by affecting Q-factor and also independent of Q-factor; the different surface morphologies and surface chemistry resulting from different fabrication techniques begin to play a large role in the power required for plasma breakdown. This finding suggests that field emission is likely playing a role in plasma breakdown. Furthermore, the predictability of breakdown is also influenced by surface morphology and chemistry. In all, it is found that an order of magnitude variation in breakdown power performance can result from variation in Q-factor, surface morphology, and surface chemistry. Chapter 5 discusses future avenues of research by which surface morphology and chemistry may be used to reduce breakdown power.
Chapter 2

A Novel, All-Dielectric, Microwave Plasma Generator Towards Development of Plasma Metamaterials

Around the turn of the century theorists began predicting what seemed like science fiction, invisibility cloaks and super lenses capable of focusing beyond diffraction limits [4-5]. The key to achieving such feats was metamaterials, engineered structures for controlling permeability and permittivity. Shortly following the theory, metamaterials were experimentally demonstrated and met with much enthusiasm [6-7]. New exciting properties such as perfect absorbing materials were also predicted and demonstrated [8]. However, current metamaterials have limitations. One prominent limitation is the small bandwidth over which metamaterials operate. As a result, many attempts have been made to produce tunable metamaterials via mechanical, electrical, or a variety of other types of tuning [9]. Plasmas became interesting candidates for metamaterials because their permittivity can be changed dynamically; this means that a plasma metamaterial can be tuned to a desired frequency. Such tunability could allow, for instance, negative refraction over a very broad band, from GHz to THz, through changes in parameters controlling plasma properties such as pressure, gas type, or input power [10].

In order to make plasma metamaterials a reality, it is imperative to be able to generate and sustain plasmas with controlled properties and/or geometries. For instance, plasma rings and rods could be generated to replace or function with the metal structures used in earlier metamaterials [11]. In 2014, split-ring resonators, previously utilized in some of the first metamaterial structures [7], were used to generate an array of plasmas, which could perhaps be used as a plasma photonic crystal/metamaterial [3, 12]. One may think of the previously mentioned device as an instance of a metamaterial generated by another metamaterial. However,

it has also been shown that metamaterials, in this case for negative refraction, could be made completely of dielectrics and, from this, we drew inspiration [13]. Additionally, in analogy to ring resonators, it may be possible to use the resonance of dielectric resonators to tune permeability, although this possibility is not explored here.

Here, we make the first foray into all-dielectric plasma generators based on a single resonator mode for use in plasma metamaterials. It has been suggested that a high Q-factor allows for the ability to start and operate a plasma efficiently [14]; dielectric resonators can have Q-factors that are orders of magnitude larger than metal ring resonators, and therefore, may also be valuable in generating plasmas for use in plasma metamaterials. The efficient use of energy by dielectric resonators has, in the past, made them useful as filters and antennas at higher frequencies, which suggests these generators should be wirelessly operable [15]. Unlike metals, dielectrics can have low power loss at high-frequency and can have low reflectivity, which makes dielectrics suitable for low-loss interactions with GHz–THz radiation. Like split-ring resonators, our generator functions based on sub-wavelength energy localization via a halved, dielectric resonator. Thus, the present design adds a new class of generator to the existing plasma generator flora, which are discussed in several reviews [16-21]. Unlike all-previous plasma generators, the all-dielectric design of our generator makes it ideal for interactions with high-frequency electromagnetic waves.

The all-dielectric plasma generators described in this chapter were studied using computational and experimental methods. Computational results were obtained through the use of the Eigenmode, Time-Domain, and Frequency-Domain solvers of the commercial electromagnetic software, CST Microwave Studio. Cylindrical dielectric resonators (height × diameter = 13.93 × 27.86 mm) composed of Zr_{0.8}Sn_{0.2}TiO_{4} (ZST) were fabricated, characterized, and then halved resulting in the plasma generating structure (Fig. 2-1). The properties of the resonators and halved resonators were analyzed using an Anritsu 37369D vector
network analyzer; the resonators/halved-resonators were positioned in a Hakki-Coleman configuration between loop probes for magnetic coupling to the $\text{TE}_{015}$ mode [22-23]. To generate a plasma, the device was subjected to 2.45 GHz in a multi-mode microwave under ambient air conditions.

Figure 2-1: A halved ZST dielectric resonator is shown here next to a pen for a size comparison.

The concept behind the all-dielectric plasma generator is to store and leak the electric field from a resonating mode out of the dielectric and into a lower permittivity environment. The halved dielectric resonator allows the electric field of a $\text{TE}_{015}$ to enter air through a perpendicular interface resulting in an increase of the electric field amplitude by a factor of the permittivity of the dielectric. Recently, researchers have tried a similar approach [24], but our generator operates using a single mode instead of two; is more robust and easier to fabricate since no metallization is required or present to be degraded by plasma; will not suffer from conductor losses; and directly benefits from the increase in electric field associated with the dielectric interface. Figure 2-2 was generated computationally and illustrates the $\text{TE}_{015}$ and $\text{HEM}_{128}$ modes in the cylindrical resonator (a, c) and the halved cylindrical resonator with a 100$\mu$m gap separating the halves (b, d). The gap in the resonator does not appear to disturb the $\text{TE}_{018}$ or $\text{HEM}_{128}$ vector fields’ general shapes in the simulation. It can be seen in Fig. 2-2b, d that the field within the air gap of the
halved resonator is about 40 times greater than the field in the adjacent dielectric, which corresponds to the permittivity of the dielectric. Furthermore, the models of our generator indicate that, not only do the fields in the gap increase by a factor of the permittivity (Fig. 2-2), but also that the maximum field in the center of the gap (Fig. 2-3b) is larger than the field in the center of the non-split resonator (Fig. 2-3a) by about a factor of 15 as demonstrated using the TE$_{01\delta}$ mode. Electric fields as high as $10^7$ V/m are achieved in simulation using a plane-wave excitation with average incident power of 1000 W using the HEM$_{12\delta}$ of a halved resonator with 100-$\mu$m gap; the HEM$_{12\delta}$ mode, produces about 18% higher electric fields than the TE$_{01\delta}$ mode.

![Figure 2-2:](a) CST Microwave simulations of the central plane of the dielectric resonator show both the magnitude and direction of the electric field distribution of the fundamental TE$_{01\delta}$ mode. (b) This image, also produced using CST Microwave, utilizes a dB scale in order to highlight the large increase (~40×) of electric field magnitude in the gap of a halved-resonator relative to the adjacent dielectric. (c) and (d) Show the same information as Fig. 2-2a and Fig. 2-2b, for a higher-order mode, the HEM$_{12\delta}$ mode.
In order to understand the behavior of the electromagnetic mode in the halved resonator, the fundamental (TE$_{01\delta}$) resonant frequencies of the halved resonator were studied with several gap sizes and probe angles. The gaps in the resonator were produced by inserting shim stock between the halves of the resonator and then removing the shim stock. As shown in Fig. 2-4, the resonant frequency of the device increases rapidly with small (100 µm) gap changes. Error bars in the figure are based on the standard deviation from re-setting the gap and re-measuring at least two times. The large error bars in the beginning (gap sizes of 0 mm and 0.02 mm) indicate the difficulty in producing and preventing small gaps and the device’s sensitivity to small variations when utilizing small gaps. The change in resonant frequency due to gap size decreases with increasing gap distance. In particular, the trend changes markedly after 0.33 mm, and this is also near where experimental results deviate from computational results. With a 0.33-mm gap, the resonant peak in the vector network analyzer began to split into two separate peaks, suggesting the existence of two separate modes instead of one single TE$_{01\delta}$ mode as indicated in Fig. 2-4.

Figure 2-3: (a) Simulated electric field magnitude (V/m) of the TE$_{01\delta}$ mode in the central plane of the resonator with no gap. (b) Electric field magnitude of the TE$_{01\delta}$ mode in the central plane of the halved-resonator with gap size of 100 µm. The magnitude of the electric field in the halved resonator is enhanced by a factor of approximately 15 relative to the resonator with no gap.
The formation of another mode at nearly the same frequency of the TE\(_{016}\) mode may explain the discrepancy between experiment and computation. At gap sizes above 0.33 mm, the resonant responses appear to be convoluted into a single peak, which is represented here as a single frequency. The optimal operating gap distance and, thus, tunability of resonant frequency for this device is, therefore, likely situated at gap distances greater than 0.04 mm (small error bars) and below 0.33 mm (to avoid change in modal behavior). Figure 2-5 shows the Q-factors that correspond to the measurements of frequency in Fig. 2-4. A similar trend is seen in Q-factor, where the slope begins to flatten near 0.33 mm — further evidence of the existence of a different mode. The Q-factor for zero gap is very similar to previously reported values of ZST using this configuration [25]. The high Q-factors here suggest much better energy utilization as compared to ring resonators (Q ~ 100–300) [14]. Due to losses as a result of the dielectric’s contact with metal in the Hakki-Coleman setup, a technique similar to that used by the National Institute of Standards and Technology was employed for determining dielectric loss [26]. Accordingly, a resonator is suspended in a metal cavity and the Q-factor of the TE\(_{016}\) resonance is found to be approximately 12,000, which corresponds to a loss tangent (\(\tan\delta\)) of \(8 \times 10^{-5}\). From previous reports on ZST, one can determine similarly low loss tangents at 2 GHz (\(\tan\delta \sim 6 \times 10^{-5}\) ) [27].

Figure 2-6 shows the variation in resonant frequency due to changes in excitation angle. That is, we rotate the device between the two probes as shown in the inset of Fig. 2-4. A probe angle of zero degrees corresponds to exciting the device with the probes perpendicular to the gap. The stability of the resonance frequency with probe angle suggests that different angles of coupling do not change the response of the device. The stability of resonant frequency means the device can be predictably excited from various angles, which can be helpful in a multi-mode microwave cavity or when operating the device wirelessly. Since the plasma may also take on the geometry of the gap, this could also allow for one to orient plasma sheets as desired by rotating the halved resonators.
Figure 2-4: Experimental and computational results of the resonant frequency of a halved resonator with various distances between the halves. Single-mode and double-mode regions are distinguished. Computational results show a similar trend as measurements, especially within the first 0.25 mm. The inset of this image shows a drawing of our experimental setup looking from the top down. Resonant behavior is studied as a function of gap size and angle $\theta$ relative to the probes. Metal plates are placed above and below the resonator (not visible in drawing).

Figure 2-5: The quality factor, Q, was measured as gap size was varied from 0 to 2 mm. The Q-factor drops precipitously until a gap size of about 0.3 mm, which corresponds in Fig. 2-4 to the two-mode region. Q-factor is determined by dividing the resonant frequency of the TE$_{01\theta}$ mode by the 3-dB bandwidth of the resonant peak when using a measurement technique developed by Hakki and Coleman and modified by Courtney [22-23].
As a final demonstration, a device was tested in a 2.45-GHz multi-mode microwave cavity utilizing the dielectric resonator’s HEM_{12δ} mode, which has a free-space resonant frequency of 2.6 GHz. The device required 1000 W of multi-mode power in order for the plasma to ignite in ambient air (Fig. 2-7), but the plasma was sustainable at 300 W, the minimum power of the microwave source. The breakdown strength of air is 3 MV/m, which should be exceeded by our resonators (~10 MV/m max field) at 1000-W average power. The extra power requirement, when comparing experiment and computation, likely occurred due to several factors including lack of resonant frequency match; energy input into electromagnetic modes in the microwave cavity which may not couple well to the HEM_{12δ} mode; and the varying dielectric properties caused by heating of the ceramic due to high-power microwaves. Our device has the additional difficulty that the gap must be set perfectly or the resonant frequency could easily vary.
by 5–10 MHz as seen in Fig. 2-4. For this material and geometry, the loaded Q-factor also broadens in free space, which in this case actually helped ameliorate problems associated with frequency matching. Many of the aforementioned problems could be rectified with a tunable microwave source.

In Fig. 2-7 the plasma is visible along with the resonator. Originally the plasma had a purple glow, but it transitioned into an orange color. We suspect the color change is caused by the presence of impurities due to the destruction of the ceramic. Upon excitation, the plasma appeared to cover a large fraction of the area between the resonators, and filamentation was not visible. The plasma was sustained for several minutes as the power was decreased from 1000 W to 300 W. Future work will include characterization of the plasma for this new type of generator, but we expect the plasma to be similar to previously reported capacitively-coupled, microwave microplasmas, which had plasma densities and electron energies consistent with glow discharges — our models show similar expected electric field strength (corresponding to ~100–300 V) in similar gap sizes [14, 28-29]. Similarly, in a very recent paper, the excitation of plasma using dual-dielectric resonators was demonstrated [30]. Looking closely, one can see that our device was actually destroyed, likely due to the high microwave power, typically used for microwave sintering.

Figure 2-7: Shown here is the halved-dielectric resonator through a window in the microwave chamber. The resonator is circled in black and a black arrow points to the plasma that formed in the gap of the resonator (marked with a black, dashed line).
We have designed, characterized, and provided a proof-of-concept of a new type of microwave plasma generator. We have explored properties that will help inform the design of newer, finely-tuned devices. This type of generator has the potential to operate very efficiently due to high Q-factor dielectrics and lack of conductor losses; simulations suggest the generator may provide high electric fields (~10^5 V/m) with low power input (1 W) and even smaller losses in the dielectric, which is useful when considering an array of devices in a low pressure argon environment. In addition, the generator can be operated wirelessly and can be miniaturized through the use of high permittivity materials. There is much room for exploration in this class of plasma generator through the use of different geometries, materials, and modes, which may increase their viability in applications such as plasma processing, plasma transistors, plasma metamaterials, high-efficiency lamps, and so on. Future work will include the design of new materials, plasma characterization, and different devices via expansion of the concept.
Chapter 3

Material Influence on GHz Split-Ring Resonator Plasma Ignition Performance

3.1 Introduction

Non-equilibrium plasmas have found exciting application in a wide swath of fields including materials processing and synthesis [31-32], wound healing and cancer treatment [33-34], decomposition of greenhouse gases [35-36], and tunable metamaterials [10]. The type of plasma and method of generation are similarly broad with pressures ranging from mTorr to greater than atmospheric pressure and electrical stimuli from DC to microwave. Of particular interest for this work are microplasmas generated using microwaves. Microwave-driven microplasma generators have been under study for over a decade and have many advantages over other types of plasma generation [21]. For instance, microwave plasma generation has been demonstrated using voltages lower than that predicted by Paschen’s Law [14, 29]. In addition, microwave plasmas can produce high electron densities [21, 37], can be remotely excited [3], and typically cause less damage from sputtering than plasmas produced at lower frequencies and DC [21, 28, 31]. These plasma generators have typically utilized metal resonators, but recently dielectric resonators have also been used successfully for plasma generation [30, 38]. It is believed that the Q-factor plays an important role in breakdown [29], but no comparative studies between materials have been performed to confirm the role of Q.

In addition, these microwave microplasma devices often utilize a small gap spacing of ~100 µm or less, which allows efficient generation of plasmas at higher pressures [28, 29, 39]. In DC plasma generators using microscale gaps (~10 µm) and polished electrodes, non-Paschen behaviors

have been reported [40-41]. These behaviors have typically been attributed to ion-enhanced field emission, but gap sizes are generally limited to 10 \( \mu \)m or less for this behavior [42]. This requirement is due to the high electric fields produced in small gaps, which are necessary for field emission. However, field enhancement due to rough surfaces or intentionally designed structures such as nanotubes can reduce the macroscopic field required for field emission [42-44]. In addition, there is some evidence that RF plasmas using larger gaps have produced field-emission effects [36, 45]. It is believed that these effects will continue to become more relevant at even higher frequencies at which secondary electron emission can play a smaller role. However, other authors claim that the behavior is not due to field emission but due to having many effective gap sizes [46].

In complex electrode configurations, for which there are many different gap spacings, Paschen’s law appears to be violated as a result of the discharge being optimized at values that are different than the minimum gap spacing [47]; this phenomenon of long-path breakdown is likely a factor in configurations such as the split-ring resonators used in our study. Despite a significant amount of exploration at lower frequencies and DC, not much has been done regarding the importance of charge emission processes for microwave microplasmas.

Studies of breakdown mechanisms in microplasmas using microwaves have been primarily limited to simulations. Three regions of different behavior have been identified recently: the boundary-controlled regime, the diffusion-controlled regime, and the inertia-controlled regime [48]. Classically, the diffusion-controlled regime has been well-studied [49-51]. This regime is characterized by high collision rates; thus, the electron mean free paths are small relative to the electrode spacing, and interactions of ionized species with the walls other than diffusional losses are ignored. The inertia-controlled regime is a continuation of this behavior but at high frequencies at which smaller particle motion leads to a need for more energy to trigger breakdown. The boundary-controlled regime, which occurs at the lowest frequencies, is characterized by interactions of charged species with the electrodes and the subsequent emission/absorption of
electrons. The dominance of field emission, secondary electron emission, and electron impact ionization on breakdown depend on the breakdown regime and on the gap spacing [52-53]. In all regimes, the selection of electrode material should play an important role in the plasma ignition power due to resonant characteristics [29], but in the boundary-controlled regime the material may also influence the breakdown mechanisms. Again, a comparative study of electrodes for microwave microplasma generation could be useful.

Presented here is the first comparative experimental exploration of the effect of electrode materials, specifically Ag and Au, on the plasma ignition performance of resonant, microwave microplasma generators. These metals appear to be good candidates for study since they have different work functions, 4.6 eV for Ag and 5.3 eV for Au, and different conductivities, $4.5 \times 10^7$ S/m and $6.3 \times 10^7$ S/m for Ag and Au, respectively. [54] It is estimated that secondary electron emission is roughly proportional to work function in metals, [48, 51] and such proportionality suggests that Ag may have an advantage in breakdown in the boundary-controlled regime. Field-emission contributions could result in lower breakdown for Ag devices relative to Au devices as well. In addition, the difference in conductivity will give us a direct platform with which to study the effect of Q-factor. Ultimately, by using these materials, we seek more generally to explore the factors that influence microwave microplasma breakdown.

3.2 Experiment

A drawing of our experimental setup for studying plasma generation is shown in Fig. 3-1a. The stainless-steel vacuum chamber holds approximately 14 L and can be pumped to a base pressure of 50–70 mTorr using an oil-free roughing pump. An HP 8752C vector network analyzer (VNA) is used to measure split-ring resonators (SRR) microwave properties in the vacuum chamber; the VNA is also used as a continuous, single-frequency, microwave source for plasma
ignition. Additional microwave characterization is performed using an Intercontinental microstrip fixture and an Anritsu Lightning 37369D VNA, which is capable of higher accuracy after calibration. For plasma ignition tests, the continuous, single-frequency VNA signals are amplified using a 16-W Mini-Circuits microwave amplifier (model ZHL-16W-43-S+).

A Mini-Circuits directional coupler (model ZFBDC16-63HP-N+) is used to separate approximately 1.6% of incident and reflected power for measurement using Mini-Circuits power meters (model PWR-6GHS+). Attenuators are used to reduce the signal to power meters by 10 dB to protect them from power overload. The power meters are self-calibrating for changes in room temperature and additional calibration is considered for attenuators and frequency-dependent losses in the directional coupler; losses in coaxial cables and adapters between different microwave connectors are also accounted for after measurement. Vacuum measurements are made using a Terranova 926 Dual Convection Vacuum Gauge controller and a Duniway CVT-275-101 convection-enhanced Pirani gauge.

Screen printing is explored as a method for fabricating SRRs such as those shown in Fig. 3-1b and 3-1c. Screen printing is an additive process that requires no chemical etching; it is advantageous in that circuits can be made quickly and cheaply relative to other techniques such as using copper-clad laminates and with low losses up to 18 GHz [55]. In addition, this technique typically produces thick films (~10 µm), which significantly exceed the skin depth (1.2–1.5 µm) of Ag and Au. Resonators of Ag and Au are fabricated using ESL9912-K-FL and ESL 8844-G inks on 96%-pure alumina substrates from CoorsTek. All SRRs have Ag ground planes with the exception of sample H1, which is discussed in the next section. Rings are dried at 120 °C for 15–20 minutes and fired at 850 °C in a belt furnace for a total duration of 15 minutes.

The SRRs were designed following guidelines from previous work and through use of CST Microwave Studio [29]. The microwave properties are given in Table 3-1. The highest value of $S_{11}$ is $-8$ dB which is equivalent to 84% transmitted power on the least impedance-matched
sample. The characteristic impedance of the SRRs is 50 Ω but the input impedance depends on a variety of factors such as the angle of the gap in the SRR, the gap size, and the Q-factor [29]. Our screen-printing mask is optimized for Ag rings and this is why they generally have a lower $S_{11}$ at resonance. The differences in $S_{11}$ lead to more or less reflection of power and this is accounted for with the power meters.

Figure 3-1: (a) A schematic of our experimental setup for plasma ignition tests. (b) A typical Ag SRR fabricated on a 25.4 × 25.4 mm 96% purity alumina substrate. Substrate thickness and line width are both approximately 0.65mm. The outer diameter of the ring is 7.4 mm. An approximately 100-µm gap is visible 10 degrees off-axis from the center of the ring. (c) An Au SRR used for generating plasma in Ar at 100 Torr is seen through the vacuum chamber window. Brass shims are used to help fix the SRR in position.

The plasma ignition power of SRRs was recorded for power levels that were capable of igniting the plasma through visual observation. The recorded power was such that there was no visual delay between the time that the power was applied and the time when plasma was formed.
This power was found to be near that at which a continuous ramp would cause plasma ignition, but pulsing and incrementally increasing the power produced more consistent breakdown voltages than ramping the power continuously. In addition, pulsing the power to ignite plasma better simulates the environment of applications such as reconfigurable metamaterials where the plasmas may be quickly cycled [10]. No spikes in power were observed when turning the signal on/off with a resolution of 20–30 ms. Plasma ignition was repeated at least five times at each pressure and SRRs were also measured throughout the pressure range at least two times. The order of data taken was also reversed with various checks to ensure that chamber conditions were not changing (e.g., outgassing) throughout a sweep of pressure. The presence of plasma was found to influence the power meters, so the recorded data was taken at a power 0.1 dBm lower than the true ignition power. This reduction of power is accounted for in calibration. The Ar pressure was held constant during tests by sealing the vacuum chamber and, thus, leaving the gas static at each pressure.

**Table 3-1: Properties of split-ring resonators.**

<table>
<thead>
<tr>
<th>SRR</th>
<th>Material</th>
<th>Q-Factor</th>
<th>Gap Size (µm)</th>
<th>Frequency at Resonance (GHz)</th>
<th>S&lt;sub&gt;11&lt;/sub&gt; (dB) at Resonance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ag</td>
<td>146 ± 3</td>
<td>95 ± 11</td>
<td>2.687</td>
<td>−13</td>
</tr>
<tr>
<td>2</td>
<td>Ag</td>
<td>147 ± 3</td>
<td>97 ± 8</td>
<td>2.693</td>
<td>−15</td>
</tr>
<tr>
<td>3</td>
<td>Ag</td>
<td>150 ± 3</td>
<td>98 ± 15</td>
<td>2.699</td>
<td>−17</td>
</tr>
<tr>
<td>4</td>
<td>Au</td>
<td>102 ± 2</td>
<td>108 ± 17</td>
<td>2.706</td>
<td>−11</td>
</tr>
<tr>
<td>5</td>
<td>Au</td>
<td>96 ± 2</td>
<td>99 ± 6</td>
<td>2.691</td>
<td>−8</td>
</tr>
<tr>
<td>6</td>
<td>Au</td>
<td>93 ± 2</td>
<td>100 ± 11</td>
<td>2.689</td>
<td>−8</td>
</tr>
<tr>
<td>7</td>
<td>Au</td>
<td>99 ± 2</td>
<td>102 ± 11</td>
<td>2.694</td>
<td>−9</td>
</tr>
<tr>
<td>H1</td>
<td>Ag/Au</td>
<td>101 ± 2</td>
<td>91 ± 13</td>
<td>2.727</td>
<td>−14</td>
</tr>
</tbody>
</table>

Rings 1-7 have Ag ground plane.
Ring H1 has an Au ground plane.
To measure the conductivity of the fired inks, we screen print ground planes of Au and Ag on alumina substrates. Next, we utilize the Hakki-Coleman method, as modified by Courtney, to measure the Q-factor of a cylindrical dielectric resonator [23]. By measuring the difference between the Q-factor of the dielectric when it resonates between bulk Ag plates and when it resonates between alumina substrates coated with Au or Ag films, we can determine the microwave conductivity of the fired inks. This technique has previously been used to determine the conductivity of various metals and carbon nanotubes at microwave frequencies and more details can be found in that work [56]. To make our measurements, we used a BaTi₄O₉ dielectric resonator with a relative permittivity of 36 and utilized the fundamental TE₀₁₁ mode which resonates at 7 GHz and has a very low loss tangent, tanδ = 2 × 10⁻⁴.

3.3 Results and Discussion

3.3.1) Structural Characterization

Scanning electron microscopy (SEM), optical microscopy, and optical profilometry were used to characterize the SRRs. A typical Ag SRR is shown in Fig. 3-2(a, c) and a typical Au SRR is shown in Fig. 3-2(b, d). From the SEM images, the surface porosity of the Au rings appears to be greater than that of Ag rings. This correlates well with optical profilometry measurements of root-mean-square surface roughness which are found to be 1.8 ± 0.07 μm and 1.2 ± 0.1 μm for Au and Ag SRRs, respectively. These surface roughness values are relatively similar, but it has been found that porosity can contribute to the decrease of secondary electron emission [57], and the increase of roughness in Au SRRs could potentially produce a larger field-enhancement factor for consideration in field emission.
Figure 3-2 also shows that the screen-printed SRRs are not uniform either at the gap or along the edges of the ring. The variations in gap size were measured using optical microscopy and are presented in Table 3-1. As seen in the table, the standard deviations for the gap are \( \sim 10\% \). This deviation is due to both the finger-like non-uniformities and also because gaps were not printed with perfectly parallel edges. The thickness of the rings was also measured using optical profilometry and found to be \( 6.3 \pm 0.6 \) µm and \( 7.9 \pm 0.7 \) µm for Au and Ag rings, respectively; the skin depth of bulk Ag and Au are 1.2–1.5 µm for comparison.

3.3.2) Plasma Ignition

Three Ag SRRs and four Au SRRs were tested for plasma ignition performance through a pressure range of 4–100 Torr of Ar. In Fig. 3-1(c), an Au SRR is shown with a plasma formed with 100 Torr of Ar. The filamentary behavior of Ar plasmas at higher pressures has been reported previously [58-60]. The length of the filaments can be controlled by reducing the input power. At pressures of 50 Torr and lower, filamentation is not seen and the plasma becomes more
diffuse as it grows in size. However, more diffuse filaments have been observed by applying power levels that are appreciably greater than required for breakdown near 15 Torr. The causes for this are currently unknown but appear to be related to an excess of voltage. Although the primary plasma properties have not been characterized, similar devices have been extensively characterized in the literature. These works suggest an electron density ranging from $10^{11}$ cm$^{-3}$ at 100s of mTorr up to $10^{14}$ cm$^{-3}$ at atmospheric pressure [21, 29], an average electron temperature of 1–2eV [29, 60], and a gas temperature ranging from 400-1000K [21, 61]; discharges on larger rings (~2 mm microstrip width) showed lower temperatures in earlier studies [14].

The ignition power average of Au and Ag SRRs, which were excited at their resonant frequencies, is shown in Fig. 3-3. The performance of Ag resonators is seen to be both more consistent and superior relative to the Au resonators. The consistency, as described by the error bars given by standard deviation in Fig. 3-3, is likely related to the structural uniformity as the Q-factor also varies more among Au rings as seen in Table 3-1. The variation in ignition performance is seen to be greater at the highest and lowest pressures. We believe that this is occurring for two reasons: 1) specific features of each ring (e.g., gap size and variations) influence the performance more when not in optimal plasma ignition conditions and 2) as power is increased, the resonant frequency of the rings shifted slightly, likely due to heating, and changed the plasma ignition performance. For instance, a ring with a smaller gap may have better performance at high pressure than one with a larger gap and thus, even though they may perform similarly under optimal pressure at 15 Torr, this is less true as pressure rises. This variation in slope of ignition power with changing pressure was observed previously when the gap size of SRRs was varied [29].
3.3.3) Q-factor and Plasma Ignition Performance

In order to understand the plasma ignition performance, it is important to characterize the Q-factor of SRRs, which is typically defined as a ratio between energy stored per cycle and power loss. A high Q-factor allows standing waves to build up in a resonator, which means a large electric field will be present in an SRR’s gap. The influence of Q-factor on plasma ignition has been derived previously and can be expressed as [29]:

\[ V_{\text{gap}} = 4 \sqrt{Z_0 Q P_{\text{in}} / \pi}, \]  

(3-1)

where \( V_{\text{gap}} \) is the maximum voltage between the electrodes, \( Z_0 \) is the characteristic impedance of the microstrip lines, \( Q \) is the quality factor of the device, and \( P_{\text{in}} \) is the net power input to the SRR. Several different techniques were explored for determining \( Q \). In the case of plasma generation, the loaded \( Q \) is relevant since the resonant device cannot operate independent of external circuits.

One commonly used technique to determine \( Q \) is to divide the resonant frequency by the 3 dB bandwidth of \( S_{21} \) or \( S_{11} \), as has been applied to both ring [14] and dielectric resonators [23, 38]. We utilized both \( S_{11} \) via the microstrip, and used a loop probe (at various locations and with low \( S_{21} \) magnitude to prevent loading of \( Q \)-factor) to determine \( S_{21} \) in order to apply these techniques. Another similar technique, derived for parallel resonators, involves determining \( Q \) from the resonance and bandwidths (multiplied by a geometric factor) from a circular response produced by resonators in a polar plot of the reflection coefficient or in a Smith Chart [62]. This \( Q \)-circle technique is useful for determining a degree of uncertainty in \( Q \) since the resonant frequency–bandwidth ratio is multiplied by a correction factor depending on where the points are chosen on the circle; thus, the various values of \( Q \) determined from multiple points gives a range of \( Q \) values. We found that these techniques produced very similar results (within ~5%). We also
employed a technique of finding $Q$ based on the bandwidth of the magnitude of impedance for series resonators [63]. Finally, $Q$-factor was also found using a non-linear curve-fitting scheme as has been done in previous studies by another group [64]. The last two techniques produced significantly different results from the first two (factor of ~1.5), suggesting an indirect measurement of $Q$ based on microwave conductivity could be useful. Ultimately, we will be interested in the ratio of $Q$-factor for Ag and $Q$-factor for Au SRRs and measurements of conductivity will be useful here as discussed below.

![Figure 3-3: The ignition power of SRRs as a function of pressure. Both rings exhibit a Paschen-like behavior in which one minimum exists and the concavity of the curve does not change.](image)

The microwave conductivity of the fired Au and Ag inks were found to be $2.6 \times 10^7$ S/m and $5.7 \times 10^7$ S/m, respectively. The bulk conductivity for Au is $4.5 \times 10^7$ S/m and bulk Ag has a conductivity of $6.3 \times 10^7$ S/m. The Au ink is found to deviate further from the bulk values than the Ag ink. As discussed in section 3.3.1, the Au ink shows both more porosity and surface roughness and we believe that these factors reduce the conductivity.
We can use the conductivities to help us determine the best way of measuring the Q-factor. To do this we utilize a series LCR circuit to model our SRR at the resonance of interest — a characteristic of a series resonator is a minimum in impedance at the resonant frequency and this is observed at the resonance we use for generating plasmas. The Q-factor is then given as [62-63]:

$$Q = \frac{\omega_0 L}{R}, \quad (3-2)$$

where $\omega_0$ is the resonant angular frequency, $L$ is the inductance of the circuit, and $R$ is the resistance of the circuit. In our case $L$ and $\omega_0$ should not vary from ring to ring since they depend on the microstrip geometry, which is the same for Au and Ag rings. For $R$ we use the expression for high-frequency waves traveling on a conductor [65]:

$$R = \sqrt{\frac{\omega_0 \mu}{2 \sigma}}, \quad (3-3)$$

where $\mu$ is the permeability of the conductor and $\sigma$ is its conductivity. Now, by using Equation 3-3 in 3-2, the ratio of Q-factors of two resonators will reduce to the ratio of conductivities. In our case, the ratio of the Q-factor of Ag and Au from conductivity is found to be 1.48. This ratio is in good agreement with the ratio found using our impedance measurements of Q-factor, which is 1.52. Table 3-1 shows Q-factors as determined using the impedance measurements. Using the 3-dB bandwidth/Q-circle method a ratio of 1.32 was found. The non-linear-curve fitting technique produces values similar to the impedance measurement, but we found this technique to be less precise and more subjective; curves generated with $Q$ that varied by almost twice the uncertainty of $Q$ in the impedance method fit well.

In order to directly test the validity of Equation 3-1, we assume that an SRR with similar gap size, regardless of material, should produce the same gap voltage at breakdown. With this assumption, we calculate the expected ratio of ignition power between Au and Ag resonators and plot this result along with the recorded power ratio as shown in Fig. 3-4. The expected power
ratio is determined by taking the ratio of the average Q-factor for Ag resonators and Au resonators since Q-factor and $P_m$ are inversely proportional. The uncertainty is determined using error propagation in quadrature of the measurement uncertainty in Q from impedance measurements for Au and Ag SRRs. The uncertainty in the measured power ratio is due to error propagation of the standard error of ignition powers for Ag SRRs and Au SRRs. The standard error of Q-factor was less than the measurement uncertainty from the impedance measurement of Q as a result of the VNA frequency resolution. The observed and expected power ratio align very well. This agreement provides the first direct experimental evidence of the validity of Eqn. 3-1 and suggests that the main driving factor behind performance of SRR plasma generators is Q-factor. However, an upward trend appears to be present in the power ratio data. We believe that this is occurring since the Au SRRs on average have a slightly larger gap size than the Ag resonators. A pattern where SRRs show a decreased slope of power over pressure for smaller gap sizes has been observed before. [29] These relatively small deviations away from the expected power ratio were also seen when performing this analysis on SRRs of the same materials. Averaging over several SRRs helps separate the effect of the material from the differences due to fabrication variability such as gap size, gap size variation, thickness variation, and surface features.

To further isolate the Q-factor, an Ag SRR, which is identified as Ring H1 in Table 3-1, was modified such that its Q-factor was decreased to that of an Au resonator. This was achieved in two steps. First, Ring H1 was placed on an Au ground plane instead of an Ag ground plane and the Q-factor dropped to 129, which is near the average Q-factor of Au and Ag. It is believed that the Q-factor did not drop further since the current density on the microstrip is higher than in the ground plane. After that, Au was painted onto the side of the SRR opposite the gap, where the conduction current density is expected to be the greatest according to simulations. The SRR was dried and fired again likely resulting in a solid solution between Au and Ag in the painted
location. However, the material where the plasma is formed is far from the modified location and remains as Ag. The ignition power ratio of ring H1 vs. the average of Au rings is shown in Fig. 3-5. Again, the expected and observed ratios appear to be in good agreement. We see greater deviations at higher pressures — this is consistent with and helps support our earlier comments regarding changes with pressure due to gap size since H1 has an even smaller gap than the Ag rings tested earlier. We note that, by reducing the Q of an Ag resonator, we also have addressed the issue of different loading on Q-factor, which could arise due to the amplifier and directional coupler differing from the microstrip characterization apparatus. This experiment also addresses the issue of increased surface roughness and porosity seen with the Au SRRs relative to the Ag SRRs.

### 3.3.4) Surface Chemistry and Plasma Ignition Performance

Although Q-factor appears to play the largest role on performance between Ag and Au, we also studied the surface chemistry of our resonators using X-ray photoelectron spectroscopy (XPS) as shown in Table 3-2. As seen in the table, the as-made samples, especially Ag SRRs, had carbon contamination that is likely from environmental hydrocarbons. The plasma was found to clean carbon from the surface as shown by the decrease in carbon content for the plasma-treated Au sample. Mechanical exfoliation with a vulcanized rubber eraser was also utilized to clean Ag resonators and left traces of S. In addition, by sputtering away the top 10 nm, the sample surfaces were found to be almost pure Ag and Au. Oxidation is believed to have occurred on the exfoliated sample as the O content is high relative to the sputtered sample. An associated dark film also appears to form — this is discussed more later. This cleaning process reduced the RMS surface roughness of an Ag SRR to 0.80 ± 0.02 μm. The plasma ignition performance showed little to no change beyond uncertainty limits except at 100 Torr where the smooth sample required more
power. The standard deviation at 100 Torr was 4.5%, which is above the 3% maximum standard deviation found for remounting an Au sample. This change is likely due to modifying the gap geometry as we have seen such changes tend to be more effective at altering the ignition power at pressures that are not near the pressure for minimum ignition power.

Figure 3-4: The power ignition ratio of the average ignition power of Au rings and the average ignition power of Ag rings as a function of Ar pressure. The expected power ratio calculated from the ratio of Q-factors depends only on the conductivities of the two materials.

Figure 3-5: The ignition power ratio of the average of Au rings and H1 is plotted as a function of pressure. Here the ratio of Q-factors depends on the effective conductivity of H1, which is an Ag SRR with regions of low conductivity, and the conductivity of Au.
Like the Ag in the exfoliated sample, the Cu in the Au SRRs also became oxidized as observed by the increase in O content and the XPS signature for Cu–O bonds being present in the plasma treated sample. The Au SRRs also had trace amounts of Bi that is likely from bismuth oxide added as an adhesion-enhancing material within the screen-printed ink. Additives such as bismuth oxide and copper oxide are commonly added to help with bonding Au to ceramics and glasses [66]. Since the Au SRRs surface showed high amounts of Cu relative to Au and other oxide materials, the sputtered SRR was tested for plasma ignition performance to assess the contributions due to impurities. We found no significant difference with respect to our uncertainty limits between a sputtered Au SRR and a non-sputtered Au SRR. This suggests that these surface contaminants played a minor role in plasma ignition performance.

However, the performance of SRRs has been found to vary over multiple trials. In the case of Au SRRs, the first trial typically requires additional power. We believe that the power for ignition decreases as a result of cleaning the carbon contamination. This change contributes to the
maximum 3% standard deviation seen when remounting and retesting an Au SRR. In the case of Ag resonators, performance will eventually decrease over time as a dark (black/brown) film begins to form. We believe this film is partly silver oxide and partly silver fluoride. The fluorine contamination was not included in the XPS data, but fluorine contamination was present in all samples exposed to plasma with increasing amounts of fluorine near the SRR’s gap. In addition, silver fluoride is highly soluble (1800 g/L) in water whereas silver oxide is not (0.013 g/L) and much of the dark film can be removed using deionized water. Thus, we believe a large component of this film is silver fluoride.

Figure 3-6 shows the effect of film formation on the performance of an Ag SRRs. The power required for the Ag SRR with a film formed by plasma is compared to the same resonator without a film. The standard deviation of ±3% in ignition power from remounting is used to determine uncertainty through error propagation in quadrature. A maximum increase in ignition power of ~20% is seen for low pressures while at high pressures the changes are virtually indistinguishable.

Figure 3-6: The ignition power ratio of an Ag SRR after the formation of a dark film and the ignition power of the same Ag SRR before the film formation is shown as a function of pressure. An increase in power is evident at lower pressure but decreases with increasing pressure.
We believe that these changes can be explained by the change in the mean free path of electrons. At higher pressures, electrons are believed to be essentially trapped in the gas except for diffusion to the walls — this is the foundation for many theories on microwave breakdown and also considered in previous works on SRRs [14, 49-51]. As a result, interactions with the surface are expected to play little to no role and Fig. 3-6 appears to support this conclusion. At lower pressures, the electron mean free path increases to the point at which electrons traverse the gap and interact heavily with the electrodes. This behavior also agrees with the observed behavior in Fig. 3-6 assuming that the film has a lower secondary electron coefficient than the metal.

3.4 Conclusions

SRRs of different materials were compared for their plasma ignition performance at pressures around the optimal operating pressure for low power ignition. It was found through comparisons of multiple Au and Ag rings that the main contributing factor to ring performance is the Q-factor of the SRR, which for a fixed geometry is controlled by the microwave conductivity. Microwave conductivity measurements helped us choose the most accurate and precise way of measuring Q-factor after trials with several common techniques. This conclusion was further validated by modifying the $Q$ of an Ag SRR until its $Q$ and plasma ignition performance simultaneously approached that of an Ag SRR. Furthermore, the surface chemistry of the SRRs was studied and it was found that common surface contaminants from the atmosphere and inks contribute less significantly (~6%) to the performance of the SRRs. However, upon the formation of a visible film on the SRRs, a significant performance decrease was observed. The film was formed due to plasma exposure, appeared continuous in the plasma exposed region, and was determined through XPS to contain fluorine and oxygen. Such a film was found only to form on the Ag SRRs, and is believed to be composed of silver oxide and silver fluoride. The performance
decrease from the film was most significant for the lowest pressures and became less important as pressure was increased. Such a profile in performance is consistent with a framework in which the electron mean free path only allows significant interaction with the material surface at low pressures. This framework helps further justify the conclusion that the main material parameter influencing performance, when using materials as similar as Ag and Au with a common fabrication technique, is conductivity. This conclusion is especially true at pressures above 50 Torr. However, the change in ignition performance by 20% at low pressures suggests there is room, with the appropriate selection of materials, to improve SRR performance in this regime. Exploration into more materials and different surface morphologies, especially those which can significantly enhance electric fields, will be important in future work.
Chapter 4

Atmospheric Microplasma Breakdown and Evidence for Field Emission in Split-Ring Resonators

4.1 Introduction

For at least the past two decades, researchers have been exploring atmospheric pressure discharges that were capable of remaining in a stable, non-equilibrium state. A general scheme was to spatially confine the plasma such that one of its dimensions was limited to less than 1 mm. These so-called microplasmas have since found numerous applications in areas such as metamaterials [10], spectroscopy [67], medicine [33], and materials synthesis [68]. In addition, the techniques for producing microplasmas have been growing and have been the subject of several review articles [18, 20 69, 70-71]. Of particular interest here is the production of microplasmas using microwaves. Microwave microplasmas have many promising qualities such as minimal sputtering compared to lower frequency excitation [14], high-electron densities [21, 72], potential for breakdown at voltages less than predicted by Paschen’s Law [28], and the possibility for remote excitation. [1, 2] In addition, microwave microplasmas can be formed using generators that are comprised entirely of dielectric materials — this could provide further advantage in terms of reducing electrode degradation and additional flexibility in applications such as metamaterials for which potentially reflective metal structures may not be desirable [30, 38]. Importantly, the low device degradation and high-electron densities attainable with atmospheric-pressure, microwave microplasmas may enable plasma-based metamaterials operating at high-frequencies, thus making them viable for 5G and potentially future generations of wireless communication.

* This chapter is adapted from Z. Cohick, B. Hall, D. Wolfe, and M. Lanagan, “Atmospheric pressure breakdown probability and evidence for field emission in microwave split-ring resonators” in preparation for submission to Plasma Sources Science and Technology (2019).
One way of generating microwave microplasmas is to use split-ring resonators (SRRs) [1, 2, 14, 21, 29, 72-73], which are often associated with metamaterials. These SRRs can locally concentrate electric fields in the interelectrode gap to cause breakdown — similarly, the all-dielectric microwave microplasma generators utilize dielectric resonators which also locally concentrate fields [30, 38]. Studies of microwave SRR plasma generation have been carried out in a wide range of pressures including atmospheric pressure [1, 2, 14, 21, 28-29, 72-73]. A few papers explore variations in device materials or properties such as Q-factor and microstrip dimensions [64, 73-74]. However, studies of the influence of materials, fabrication methods, and microstructure are absent at atmospheric pressure. In addition, despite studies of parallel-plate-style microwave electrodes with varying interelectrode gaps [75-77], there is a dearth of experimental work concerning SRRs or coplanar electrodes with different gap sizes below 100 µm. The study of small gap sizes becomes especially important since field emission is expected to become increasingly more likely as interelectrode spacing is reduced.

Field emission can potentially play a large role in plasma generation and gaining an understanding of this phenomenon can be useful in either assisting or preventing breakdown. For instance, in the case of DC microplasmas, it has been found that breakdown voltage can significantly decrease relative to expectations in Paschen’s law as a result of field emission when gap sizes are reduced to ~10 µm and lower [42]. The degree of field emission can be heavily influenced by factors such as surface roughness, adsorption, presence of ions, temperature, and electrode material [42, 78]. This effect has also been demonstrated recently for pulsed plasmas [79]. In pulsed plasmas and under other conditions, such as high excitation frequencies, in which ions may not contribute much to breakdown due to scarcity and low-energy, field emission is expected to play an even larger role in breakdown [80]. There has been evidence that RF plasmas generated in gap sizes up to about 70 µm exhibited non-Paschen type behavior due to field emission [45]. However, this behavior may be related to a transition in breakdown regime from
secondary electron emission dominated by gas ionization [81], or to the effect of having multiple effective gap sizes resulting from co-planar electrodes [46, 82]. In our previous studies of microwave SRRs with gap sizes of ~100 µm it was found that field-emission was likely not playing a major role in breakdown [73]. However, simulations of microwave breakdown suggest that field emission will begin to play a role with gap sizes of 50 µm and less [48, 52]. With field emission, it may be possible not only to lower breakdown voltage requirements but also to increase electron density for a given voltage [83-84]. Although simulations have shown the possibility of field emission assisting breakdown [48, 52, 83-84], there has been no reported experimental evidence for field emission in microwave microplasma generators. Therefore, experimentation with small gap spacings in microwave microplasma generators is of interest in this work.

Figure 4-1: A screen-printed Au resonator on alumina with fs-laser-ablated gap sustaining an atmospheric pressure Ar plasma with a few mW of input power. The alumina substrate appears somewhat yellow in color owing to low-light conditions. The gap of the resonator is offset 10 degrees to match impedance to 50 Ω input. For scale, resonator diameter is 7.4 mm.
We examined plasma generation in 43 variegated SRRs in order to explore the effect of fabrication methods, microstructure, materials, and sub 100 µm interelectrode gaps, which facilitate the possibility of field emission. The focus of our study is on fs- and ns-laser ablated Au and Ag SRRs as well as screen-printed SRRs with fs-laser ablated gaps. The use of fs- and ns-laser ablation differs mainly in that ns-laser ablation is expected to be a much more thermal process, whereas fs-laser ablation can be athermal [85]. Both methods are expected to produce microstrip sidewalls with better verticality and smaller features than screen printing [86-87]. These fabrication techniques can also produce different microstructural features in the interelectrode gap. Furthering this work, we also make minor forays into other SRRs — an e-beamed Cu SRR as well as an Au SRR with CuO nanowires in the interelectrode gap. By studying different fabrication methods, materials, and interelectrode gap sizes, we seek to gain a better understanding of breakdown mechanisms that may be utilized for promoting or inhibiting breakdown and plasma generation.

4.2 Experiment

4.2.1) Equipment and Setup

The experimental setup for this study is similar to the one illustrated in our previous work on microwave SRRs [73]. Plasma generation is carried out in a 1 L cylindrical vacuum chamber using SRRs such as the one shown in Figure 4-1. This work discusses studies of 43 such SRRs with differences in material (Ag, Au, Cu, CuO), fabrication technique (see section 4.2.2), and microstructure. The chamber is first placed under vacuum and pumped for at least 5 hours using an oil-free roughing pump. Next, the chamber is flushed with Ar for 10 minutes while maintaining a pressure of 1.5 Torr to promote water desorption. A base pressure of approximately
30 mTorr is achieved with a leak rate yielding less than 1 mTorr/min pressure increase over a 5–10-minute period. The chamber is then backfilled with Ar until it reaches greater than atmospheric pressure (~800 Torr). At this point, a valve connecting the chamber to a gas bubbler system is opened, which ensures that the pressure in the chamber remains above atmospheric pressure by approximately 6 Torr. To reduce the amount of water vapor reaching the chamber, an additional container of Drierite (CaSO₄) desiccant is placed between the vessel, which contains water and the vacuum chamber. A flow rate of 70 sccm of Ar is maintained through the duration of the experiment to slowly replenish the vacuum chamber with Ar. Breakdown probability was found to be consistent for greater than 10 hours. In a larger 14-L vacuum chamber with static Ar and a similarly small leak rate, it was found that the breakdown probability slowly decreased over the same time period despite baking the chamber to remove water.

Microwave power is delivered to the chamber by a Mini-Circuits microwave amplifier with an HP 8752C vector network analyzer acting as a source. For plasma breakdown studies, the output power from the amplifier is stepped by 12.5–500 mW using LabView — see section 4.2.3 for more discussion. A Mini-Circuits directional coupler (ZFBDC16-63HP-N+) is used to sample a small portion (~1.6%) of the power incident upon and reflected by the SRR, which is subsequently measured using Mini-Circuits power meters (PWR-6GHS+).

4.2.2) Split-Ring Resonator Fabrication

All SRRs were deposited onto 96% pure alumina substrates from Coorstek. The Au and Ag were deposited using screen-printing as was done in our previous work using the same inks, ESL9912-K-FL and ESL 8884-G [73]. Screen printing allows for thick films (~10 µm) that are much greater than the skin depths of Au and Ag, which are 1.2–1.5 µm, respectively, at the operation frequency; the wet thickness of the films is typically about twice the dry thickness [88].
Average surface porosity values of 6 ± 1% and 1.2 ± 0.4% for Au and Ag, respectively, were determined from multiple SRRs using a thresholding technique on scanning electron microscopy (SEM) images. In contrast to our previous work, in which the entire SRR pattern was screen-printed, we used laser ablation to pattern the interelectrode gap and, in some cases, the entire SRR. Laser ablation allows for much finer features than that which are achievable using screen-printing [86-87]. Due to the different fabrication techniques and gap sizes, we found that the resonant frequency of SRRs in this study varied from ~2.6–2.9 GHz.

Two lasers were used to fabricate the resonators. One was a Coherent Avia 355-28 with a wavelength of 355 nm, a 30-ns pulse duration, and a maximum pulse energy of 300 μJ. The other laser was an Amplitude Systems Satsuma HP-20 with a second- and third- harmonic generator allowing output of three wavelengths; 343 nm and 1047 nm were used for these experiments. Both wavelengths had a pulse duration of 350 fs, and the pulse energies of the 343- and 1047-nm output were 8 and 40 μJ, respectively. The beam was focused and translated across the sample through the use of a Scanlab Hurryscan II-14 galvanometer scanner and associated F-theta flat-field objective. This allowed fast scanning of the beam and further minimized any local heat accumulation during the ablation process.

Processing parameters involved in these experiments were the following: pulse energy, pulse duration, wavelength, scanning speed, pulse repetition frequency, and processing method (vector/raster). Nanosecond processed samples were done with two different energies for the vectorized ablation and one energy for the rastered ablation. Because of the constant pulse frequency (100 kHz at 300 μJ) and high acceleration/deceleration of the scanner, undulating sinusoid-like surface artifacts became apparent around the edges of the SRR at vector points. To minimize this unaccounted-for morphology, a lower energy pulse energy (300 kHz at 25 μJ) was chosen to reduce these undulations and produce a more uniform output. The raster technique
produced a much more uniform surface morphology of the SRR, but at the expense of a “pixelated” edge. Because the shape was being cut out in a line-by-line fashion, all curves and features were reduced to a ~5-µm resolution.

A significant difference in the fs/ns pulse duration regimes is the deposition of heat during processing [85, 89]. Nanosecond-scale pulse durations induce rapid melting, vaporization, and even plasma formation; the effects of which have been observed in microscopy images of the samples after processing. However, femtosecond-ablated samples did not show these telltale signs, as the material-removal mechanism was different. These ultra-short pulse durations are able to deliver their energy faster than the thermal relaxation time of the material. This results in the pulse stripping electrons from the material and causes subsequent ejection of the remaining positive ions.

In addition to these screen-printed and laser-ablated SRRs, we included two other SRRs. The Cu resonator was fabricated by first E-beam depositing a ~1.5-µm Cr bond coat followed by ~30 µm of Cu in a ring pattern and subsequently using a fs laser to ablate the gap. The deposition rate was approximately 17 nm/s. To fabricate CuO we first started with a screen-printed Au SRR. Approximately 10 µm of Cu was then electroplated onto the SRR in the gap region in 3.5 minutes with a current of 0.022 A/cm² using a Caswell Cu plating bath with a pH of −1.25. The SRR was then placed into a box furnace to heat the SRR for four hours at 400 °C in air. The thermal oxidation route to forming CuO nanowires is well-explored since it is a relatively inexpensive and accessible technique [90-92].

4.2.3) Weibull Distribution

In previous studies at low-to-moderate pressure (1–100 Torr), ring resonators were found to generate plasma breakdown with good repeatability [73]. At atmospheric pressure, it has been
found that the breakdown power is much less repeatable. Previous work in microgaps using DC electrodes over dielectric substrates, as opposed to determining a single breakdown voltage, studied breakdown probability as a function of voltage [93-94]. There has also been some precedent for wide spans of breakdown voltage in a single microwave microplasma device [95]. In order to better characterize breakdown in our microwave resonators due to wide potential variations in breakdown voltage, we utilize Weibull distributions.

Weibull distributions have been used to analyze various phenomena from fiber strength distributions to breakdown in dielectrics [96]. These distributions are utilitarian — they can fit a variety of probability distributions from a Gaussian distribution to a very-skewed, non-Gaussian distribution. Two-parameter Weibull distributions are given by an equation of the form [96]:

\[ F(x) = 1 - e^{\left(\frac{x}{a}\right)^\beta} \], \hspace{1cm} (4-1)

which is defined by a Weibull or shape parameter, \( \beta \), and a characteristic value, \( a \), at a probability of \( 1/e \), which is typically near the peak of the probability density function. In our case, the Weibull distribution gives a characteristic breakdown voltage which is consistent within a few percent difference over several trials (see Fig. 4-2 and Table 4-1). The Weibull distribution within 95% confidence limits was found to fit our data well. The Statistics and Data Analysis package in MATLAB was used for finding the best Weibull fits based on maximum likelihood estimation.

To generate breakdown distributions with respect to power or voltage, we initiate breakdown in each resonator at least 30 times and up to 60 times if repeatability appeared low — i.e., if there was wide variation in breakdown power/voltage. To convert between power and voltage we utilize Equation 3-1. The Q-factor of SRRs is determined using the impedance method as discussed in our previous work [73]. Measurements of power were made at the vacuum base pressure (~30 mTorr) to prevent plasma formation; this was done since the presence of plasma
changes the power measurement. Resonators are studied both in dark conditions and with 254-nm deep ultraviolet (DUV) illumination. For each attempt at breakdown, the input power level to the SRR is maintained for 1 second and then turned off for 1 second before increasing power. For studies without DUV illumination, the amount of power that is stepped is varied from 100–500 mW. By varying step size and allowing 1 second between breakdown attempts, heating of the SRR is reduced. Reducing heating of the resonator is important since it can decrease Q-factor and change the resonant frequency [28]. In tests where our SRRs were heated due to use of high power and small step size, we observed that breakdown occurred with higher power and resonant frequency was red-shifted. Therefore, varying step size and allowing adequate cooling of SRRs was important for repeatability. The step size in power is reduced to 12.5–25 mW for studies of plasma breakdown with DUV. This reduction in step size was still not enough in many cases to produce a distribution, as opposed to a singular breakdown voltage. Further reductions in power steps were not feasible since the 1–2% output power variation from our amplifier would exceed the step size. With DUV, heating of the SRRs was not an issue since breakdown occurred with few power steps and at low power. An Ares 8-W DUV source emitting primarily at 254 nm with a secondary peak (<10% irradiance of 254-nm peak) near 182 nm (as per manufacturer specification and determined using an Ocean Optics spectrometer HR2000+ES) with minimum irradiance at surface of 5 mW/cm² was utilized (10 cm² cylindrical source with a radius of 0.85 cm).

Typically, distributions become very sharp with DUV illumination (breakdown always occurs at the same voltage within about 1 V or 0.7%), and Weibull modulus reaches values greater than 100. Removing and remounting an SRR will typically lead to a similarly sharp distribution although a change of location by a few volts has been observed. This variation may be caused by small changes in loaded Q-factor, variations in output power from the amplifier
(output power was seen to vary by 2% for the same nominal input power), and small changes in gas pressure, based on atmospheric pressure variation, and gas purity.

After breakdown, a period of two minutes is allowed before another attempt at breakdown. This waiting period is important because it was found that, if the period is shortened, the probability of breakdown was higher on subsequent breakdown attempts. Allowing two minutes reduces the dependence of one breakdown on the previous breakdown — an effect that may be the result of residual charge on the substrate or elsewhere in the chamber which then seeds subsequent breakdowns.

Table 4-1: Weibull Distribution Fits for Multiple Trials with Single Split-Ring Resonator.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Number of Breakdown Events in Trial</th>
<th>Weibull Modulus (95% Confidence Interval)</th>
<th>Characteristic Breakdown V (95% Confidence Interval)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>21 (16 – 27)</td>
<td>211 (207 – 215)</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>16 (14 – 20)</td>
<td>215 (211 – 218)</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>28 (21 – 37)</td>
<td>217 (214 – 219)</td>
</tr>
<tr>
<td>4</td>
<td>52</td>
<td>25 (21 – 31)</td>
<td>207 (205 – 209)</td>
</tr>
</tbody>
</table>

After breakdown, a period of two minutes is allowed before another attempt at breakdown. This waiting period is important because it was found that, if the period is shortened, the probability of breakdown was higher on subsequent breakdown attempts. Allowing two minutes reduces the dependence of one breakdown on the previous breakdown — an effect that may be the result of residual charge on the substrate or elsewhere in the chamber which then seeds subsequent breakdowns.
4.3 Results and Discussion

4.3.1) Breakdown Under Deep Ultraviolet Illumination

To ensure that enough seed electrons were present for breakdown, the SRR was illuminated with DUV light. In previous works it was suggested that UV radiation allowed for Townsend breakdown when intensity was less than 1 W/cm², which is much greater than the flux at the surface of the sample [94]. In DC breakdown studies in air with co-planar electrodes over insulators and microscale interelectrode gaps, the minimum breakdown voltage was similar with and without UV, but the voltage for >50% breakdown probability was reduced and the voltage breakdown distribution became narrower [94]. More recent studies on the effect of DUV on the breakdown power of DC glow discharges showed a reduction of about 10% to breakdown voltage and questioned the practical utility of DUV to breakdown studies [97]. However, other than providing seed electrons, the DUV excitation is likely to contribute little to breakdown in our case.

To help support this argument we determined breakdown voltage with the DUV source placed 3.5” and 11” from an SRR. We found that the breakdown voltage changed by about 1–2 V despite an approximate decrease of DUV flux by nearly an order of magnitude — here we assume that our approximately cylindrical DUV source is a radiator with flux decreasing as $1/r^2$, where $r$ is the distance between the SRR and DUV source. Moreover, as we will discuss in Section 4.3.3, many resonators exhibited characteristic breakdown or individual breakdown events under dark conditions at voltages that were either equal or only a few percent greater than their breakdown voltage with DUV present. This near parity in breakdown voltage occurred at gap sizes ranging from 7–100 µm and with a variety of resonators, suggesting that, at least over
this limited range, the effect of DUV is primarily to provide seed electrons and not to lower breakdown voltage.

The breakdown voltage under DUV illumination is shown in Fig. 4-3. Error bars in gap size are given by standard deviation in gap as measured using optical and/or electron microscopy. Laser-ablated SRRs typically show small standard deviations compared to screen-printed SRRs in our previous work (a few μm vs. 10 μm) [18]. Within the sets of SRRs with varying gap size (ns and fs gap), it is seen that gap size does not play a large role in breakdown voltage until gap sizes of greater than 50 μm are reached. The variation of breakdown voltage with gap size is similar to the differences between resonators with the same gap size. There are many possible reasons for this. One is that there are multiple effective gap sizes playing a role since the electric fields extend above the resonator and are not just confined to the minimum gap spacing. This allows the possibility of long-path breakdown [46, 82, 98]. Another possibility is that the breakdown voltage is relatively invariant with gap size since the breakdown conditions (gap size and pressure) are near the DC Paschen curve minimum for Ar. For instance, simulations with atmospheric pressure N₂ and small gap sizes showed that the microwave breakdown voltage followed the DC Paschen curve closely in regime 10–100 μm [52]. Yet another possibility is that the voltage in the gap as calculated using Equation 3-1 is not accurate as a result of increasing capacitance as gap size is decreased [29]. We explore this possibility further using CST Microwave Studio simulations and some transmission-line model estimations of gap voltage.

The simulated electric fields spanning the interelectrode gap for two resonators with an electrode thickness of 12μm and gap sizes of 10 and 40 μm are shown in Figure 4-4. The electric field is determined at the center of the electrodes’ cross-sections. As a result of choosing the center, edge effects and alumina-conductor-gas triple-point enhancements increasing electric field are avoided. The field is found to be symmetric showing a small decrease in magnitude towards the center of the gap. This decrease is less for the smaller gap, which better approximates a
parallel-plate electrode configuration, for which the distance between the electrodes is much smaller than the area (width × height) of the electrodes. Integrating this electric field to determine voltage gives 139 V and 135 V for the 40-µm and 10-µm resonators, respectively, with Q-factors of 160 ± 5 and 155 ± 5, respectively. This suggests that, for the same input power of 0.5 W, the resonators produce the same voltage across the gap, which is consistent with Equation 3-1. Using Equation 3-1 for one of our actual resonators with $Q = 151$, we find an interelectrode gap voltage of 139V, which is consistent with the voltages produced in simulation within 5%. The Q-factors of the simulated SRRs were determined using the same impedance method as applied to our fabricated SRRs. Thus, we find that our simulations are consistent with experiments and Equation 3-1.

![Figure 4-3](image-url): Atmospheric pressure breakdown of various SRRs in Ar vs. gap size when illuminated by DUV source. Inset shows resonators with gap size greater than 50um.

To further explore the possibility of a decrease in $V_{\text{gap}}$ compared to that calculated by Equation 3-1 as a result of increased gap capacitance, we use a transmission-line model. First, to
estimate the gap capacitance we extrapolate polynomial curves from previous theoretical work [99, 100]. The theory assumed infinitely thin microstrips, which means capacitances can be considered lower limits since additional capacitance will arise due to microstrip thickness. From this, we find gap capacitances of 0.2225 pF and 0.1305 pF for the 10 µm and 40 µm gap, respectively. Next, we utilize the fact that Equation 3-1 assumes the transmission line is terminated in an open circuit [29]. By replacing this open circuit with the gap capacitance, we find that the voltage across the gap is reduced by 16% for the 10-µm gap and 10% for the 40-µm gap. Therefore, we find that, within a few percent, the decrease in voltage due to gap capacitance does not play a large role in explaining why the breakdown voltage shows little change with gap size in the range ~10–50 µm. However, these calculations do suggest that all reported voltages that were calculated using Equation 4-2 herein may be taken as upper limits.

![Figure 4-4: The simulated electric field magnitude and voltage vs. distance of a split ring-resonator with a 40-µm gap (left) and a 10-µm gap (right). with gap size greater than 50 µm. Input power is 0.5 W.](image)

The SRRs fabricated with different methods show significant differences in breakdown voltage as shown in Figure 4-3. Since gap size up to about 50 µm was found not to be important for breakdown voltage, we can begin to consider the differences in terms of material and fabrication method. To explore this aspect of SRR performance, the breakdown voltage of SRRs with gap size less than 50 µm is shown as a function of Q-factor in Figure 4-5. It appears that
there is a slight trend towards decreasing DUV breakdown voltage with increasing Q-factor. This is unexpected according to Equation 4-2 and counter to our previous work showing that breakdown occurs at the same voltage as $Q$ is increased [73]. However, this trend appears to be more so the result of fabrication method and material than Q-factor. For instance, all SRRs fabricated using ns-laser ablation perform very similarly even as Q-factor increases by 100% when looking at the lowest $Q$ Au SRR and the highest $Q$ Ag SRR. Variation in Q-factor for SRRs of the same material is likely the result of variation in screen printing as we found previously [73]. Such variations could include inhomogeneities in metal thickness and porosity. Further variation in Q-factor is the result of variations in laser ablation associated with laser alignment/parameters, number of laser passes, presence or absence of beam expander, and raster vs. vector patterning. Variations in laser ablation can lead to differences in properties such as edge geometry (smoothness/verticality), material densification due to local heating, porosity, alumina thickness near the SRR, and melting/redeposition of alumina over the SRR. In our case, raster patterning produced lower Q-factor (<130), which is likely owing to a rougher edge geometry. The lowest $Q$ of the ns-ablated SRR was the result of a laser cleaning pass, which increased the porosity of the resonator (this SRR is discussed in more detail later). The use of different lasers also resulted in differing Q-factors — here SRRs fabricated using fs-laser ablation perform differently than those fabricated using ns-laser ablation. In the case of Au SRRs, the Q-factor of those fabricated using fs laser is lower than ns ablation, but this is not the case for Ag SRRs. As found in our previous work [73], the Au resonators show higher amounts of porosity than Ag resonators. Therefore, increases in Q-factor with ns-laser ablation may be owing to increased density on the sidewalls since ns ablation is typically more thermal in nature than fs ablation.

The fs-ablated gap Au SRRs were patterned using screen-printing with only the gap formed using laser ablation. As a result, these SRRs show Q-factors typical of screen-printed Au
SRRs [73]. Laser ablation can greatly improve Q-factor due to the presence of sharper and more vertical sidewalls and lesser variation in metal thickness towards the edges of the resonator. In this work we see $Q$ improvements of up to $\sim$100% for Au SRRs fabricated using ns-laser ablation when compared to those that are screen-printed. Returning to Figure 4-3, we see a direct comparison of a laser-ablated SRR and a screen-printed SRR, both with gap sizes of approximately 100 $\mu$m. The difference in DUV breakdown performance here is likely due to the electrode geometry as well; the screen-printed SRR decreases in thickness towards the gap and has a rounded profile whereas the laser ablated SRR maintains thickness at the gap and has a square profile.

![Figure 4-5: Breakdown voltage vs. Q-factor with DUV illumination for various SRRs in atmospheric pressure Ar. Resonators with gap size greater than 50um are not included since voltage was found to change with larger gap sizes.](image)

A wide variation is seen in the DUV breakdown voltage for resonators of different types, which we have already noted is related to fabrication differences. On further inspection we find that there may be several factors contributing to these differences. First, within any type of
resonator we see similar a range of differences in DUV breakdown V. All resonators start with a screen-printed pattern — we therefore believe that this variation can be associated with screen-printing inconsistencies such as inhomogeneities in metal thickness. This theme of thickness variation influencing performance is found in the variation of fabrication as well. For instance, the ns-laser ablated SRRs typically show deep gap trenches (>30 µm) and better performance than screen-printed SRRs with fs-laser ablated gaps, which have very shallow ablation into the alumina (typically a few µm). The e-beamed Cu SRR, which has thick (30 µm) electrodes showed similar performance to the ns-laser ablated resonators. Further variation in performance may be due to the presence or lack thereof of alumina.

Figure 4-6: Scanning-electron micrograph of a ns-ablated Au SRR (left) before and (right) after fs-laser ablation cleaning pass. The cleaning pass is seen to remove the alumina on the sidewalls of the electrodes in the gap region.

As a result of high local temperatures, the ns-laser-ablation process results in melting of both the metal and the alumina. The gap region is coated in an alumina film (typically a few µm thick). Alumina and insulators in general are known to have a high secondary electron coefficient relative to metals [101]. We believe this may be contributing to lower DUV breakdown voltages. To further explore this, one ns-laser ablated Au SRR was tested first with the alumina film present and then with the alumina film removed using a laser cleaning pass as shown in Figure 4-
6. The breakdown voltage after the removal of the alumina from the electrodes increased from 146 ± 1 V to 157 V ± 1 V. Since the gap extends significantly below the SRR electrodes into the alumina, it is possible that the alumina in this region could also be contributing to lower breakdown voltages when compared to resonators where the gap is fs-laser ablated. It may also be noted that the resonator with CuO nanowires, which are known to be poor secondary electron emitters [102], show the worst DUV performance. Therefore, we believe variation in secondary electron emission is also contributing to changes in DUV breakdown performance.

4.3.2) Breakdown Voltage in Dark Conditions

In addition to exploring the breakdown of SRRs under DUV illumination, SRRs were also tested for breakdown when in a vacuum chamber with no view ports. Figure 4-7 shows the Weibull characteristic breakdown voltage for all SRRs excluding a few SRRs for which breakdown was found to be inconsistent due to high power requirements. Again, SRRs are categorized by fabrication method. Here, we observe some trends that may be surprising.

Screen-printed SRRs with fs-laser ablated gaps are seen to show a much smaller variation in breakdown voltage when compared to ns-laser ablated SRRs. A wide voltage variation is also seen among the fully fs-ablated SRRs — this is discussed in section 4.3.3. Although the SRRs with fs-laser ablated gaps showed higher breakdown voltage when compared to ns-laser ablated SRRs, they do not change as much in breakdown voltage when in dark conditions. This is likely owing to the lack of alumina on the surface of the SRRs with fs-laser ablated gaps. These SRRs do have some alumina and Au debris, but the ns-laser ablated SRRs show a significant amount of melted alumina covering the electrodes in the gap region as shown in Figure 4-6. Later, when discussing Weibull modulus more resonators will be discussed. In addition, the metal electrodes under the alumina, such as those in Figure 4-6 (right), show a rounded profile. This is likely the
result of high temperature from ns-laser ablation and the local melting of the electrode as a result. The alumina covering the electrodes in the gap region of ns-laser ablated resonators, while it appears to help breakdown voltage with DUV illumination, is shown here to be related to not only higher breakdown voltage in dark conditions, but also wider variation. The variation could be related to several factors including the thickness of the alumina, the extent of the coverage, and damage to the alumina. For instance, in many cases, during ultrasonic cleaning of the resonators small portions of alumina were found to be removed.

![Figure 4-7: Breakdown voltage vs. gap size for various SRRs in atmospheric pressure Ar in a vacuum chamber with covered external viewport — i.e., no external light exposure.](image)

4.3.3) Weibull Modulus and Evidence for Field-Emission-Assisted Breakdown

To further explore the relationship between breakdown in dark conditions and with DUV illumination, we associate these differences with Weibull modulus and examine the
microstructure of the SRRs. Figure 4-8 shows the % increase of breakdown voltage in dark conditions over breakdown in DUV conditions vs. Weibull modulus. It is seen that, at low Weibull modulus, the breakdown voltage in dark conditions is much higher than breakdown with DUV illumination. The difference rapidly diminishes to about a 15% increase with a Weibull modulus of 25. Beyond this, the % increase continues to decrease before essentially vanishing by 40–50. To help determine the mechanism for this hyperbola-like curve we consider the microstructure and surface chemistry of the SRRs.

![Graph showing Weibull modulus vs. % increase](image)

Figure 4-8: Weibull modulus of SRRs vs. the % increase required to cause breakdown when in dark conditions compared to when DUV illumination is present. The inset shows the absolute voltage difference between breakdown under dark conditions and breakdown under DUV illumination.

Figure 4-9 and Figure 4-10 show a sample of various resonators with high and low Weibull modulus, respectively. Figure 4-9 shows SRRs in order of Weibull modulus from highest to lowest and Figure 4-10 shows SRRs from lowest to highest Weibull modulus. Tables 4-2 and 4-3 summarize some properties of SRRs shown in Figures 4-9 and 4-10. One feature shared
among high modulus resonators is the presence of field-enhancing features (FEFs). The resonator in Figure 4-9a shows surface damage due to a ns-laser cleaning pass, which was used to help remove material from the gap region without widening the gap. The electric field of SRRs with these gap sizes is about $10^7$ V/m as shown in our simulated results (Figure 4-4). On an atomically rough surface, FEFs of $\sim$1.5–115 have been reported [48, 103]. Intermediate values (50–60) are commonly used in simulations of electrodes that do not have FEFs other than that caused by atomic roughness [48, 52]. The FEFs on the SRRs in Figure 4-9 are likely capable of field-enhancement factors of greater than that due just to surface roughness, especially when considering that triple-point enhancement may also be playing a role. This suggests that the local electric field on many of these resonators with FEFs may exceed the $\sim10^9$ V/m threshold for field emission [104]. Therefore, we believe that the parity with DUV performance in breakdown voltage for these resonators is the result of seed electrons emitted by FEFs. Since the breakdown voltage on these SRRs is not lowered relative to the DUV breakdown of SRRs with fewer FEFs, we believe these field-emitted electrons are sufficient to help start breakdown, but not to contribute significantly enough to electron generation to lower breakdown voltage. This finding is consistent with some simulations in N$_2$, which suggests that field-emission can play a role in breakdown with gap sizes up to $\sim$50 µm [33]; N$_2$ breakdown voltage is about twice as high as the minimum breakdown voltage we see in Ar, but the effect could be scaled to Ar simply by halving the gap size or allowing for field enhancement factors greater than 50–60. However, other simulations suggest field emission should not be playing any role above $\sim$10–15µm in Ar [34]. At this point it is perhaps important to note that, for the SRRs with gap size 60 µm or larger, we also found higher Weibull modulus and similar breakdown voltages when in dark conditions or with DUV illumination (especially with 100-µm gap resonators). The small difference in breakdown voltage when in dark or under DUV illumination may be related to a higher collection volume for electrons that were perhaps generated by cosmic rays or which remained from previous tests.
Figure 4-9: Scanning electron micrographs (119-µm image width) of high Weibull modulus SRRs: (a) ns-laser ablated SRR, Modulus ~ 300 (b) fs-laser ablated gap SRR, Modulus: 78 (c) fs-laser ablated gap, Modulus: 45 (d) SRR w/ CuO Nanowires — inset shows higher mag of nanowires, Modulus: 40.

Table 4-3: Properties of ring resonators shown in Fig. 4-10.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gap Size (µm)</th>
<th>Weibull Modulus</th>
<th>% Increase in Breakdown Voltage Dark vs. UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7 ± 2</td>
<td>300</td>
<td>0.0006</td>
</tr>
<tr>
<td>B</td>
<td>29 ± 2</td>
<td>78</td>
<td>0.26</td>
</tr>
<tr>
<td>C</td>
<td>9 ± 2</td>
<td>45</td>
<td>5</td>
</tr>
<tr>
<td>D</td>
<td>30 ± 8</td>
<td>40</td>
<td>8</td>
</tr>
</tbody>
</table>
The SRRs in Figure 4-10, unlike those in Figure 4-9, do not have as prominent FEFs in the gap region. The worst performing SRRs appear relatively smooth and in addition have melted alumina covering the electrodes (4-10a, b, c). In Figure 4-10a the gap is extends very deep (~90 µm) into the alumina. These resonators were found to break down under DUV illumination at a slightly lower voltage than those without deep ablation into the alumina. The fs-laser ablated resonator in Fig. 10b shows less alumina, but still has a relatively smooth geometry. The SRR in Figure 4-10c is one of four SRRs that showed an intermediate Weibull modulus but a very high breakdown voltage and a large increase in breakdown voltage when in dark versus with DUV illumination. We believe this may be the result of the very high voltage required for these resonators (~400 V) to ignite, which could effectively increase the collection area for electrons above the resonator and also increases chances of field emission. The SRR shown in 10d has some more prominent FEFs and shows a higher modulus as a result. The low Weibull modulus and high breakdown voltage of these SRRs is likely owing to two factors: 1) the lack of FEFs for producing seed electrons and 2) the presence of an insulator, which can reduce the ability of SRRs to produce field-emitted electrons.

To further test the hypothesis that FEFs are contributing seed electrons we modified the resonator shown in Figure 4-9c. Testing this resonator directly after fs-laser ablation of the gap, we found a high Weibull modulus and breakdown voltage that changed little when in dark conditions or with DUV illumination. This SRR was subsequently annealed for 15 minutes at 850 °C. Microstructurally, it was found that the annealing had led to a smoothing or rounding of the FEFs. In addition, it was found that the resonator required 33% more voltage than under DUV conditions after annealing versus only 5% before and the Weibull modulus decreased from 45 to 12. This change can likely be explained by the reduction of field emission as a result of a decrease of field enhancement.
Figure 4-10: Scanning electron micrographs (119-µm image width) of low Weibull modulus SRRs: (a) ns-laser ablated, modulus: 9 (b) fs-laser ablated, modulus: 11 (c) ns-laser ablated, modulus: 19 (d) fs-laser ablated gap, modulus: 21.

Table 4-3: Properties of ring resonators shown in Fig. 4-10.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gap Size (µm)</th>
<th>Weibull Modulus</th>
<th>% Increase in Breakdown Voltage</th>
<th>Dark vs. UV</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>37 ± 3</td>
<td>9</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>40 ± 3</td>
<td>11</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>22 ± 2</td>
<td>19</td>
<td>174</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>9 ± 2</td>
<td>21</td>
<td>21</td>
<td></td>
</tr>
</tbody>
</table>
We would now like to return to Figure 4-7 and interpret it in light of our findings in Figure 4-8. In many cases, the SRRs with fs-laser ablated gaps showed FEFs. In addition, they had little visible alumina accumulation. We believe that this explains their relatively narrow range of breakdown voltage compared to the ns-ablated SRRs. In some cases, SRRs with fs-laser ablated gaps did not initially perform as well as in final tests. We believe this is due to remnant alumina that was removed after exposure to plasma. Using SEM, we correlated such changes to removal of some dark areas on the electrode near the gap. In the case of the ns-laser ablated SRR shown in Figure 4-6, the removal of alumina resulted in a large decrease in breakdown voltage (from 434 V to 274 V with breakdown under DUV occurring at 146–157 V) and, thus, provides more evidence that alumina plays a role in breakdown voltage.

The fully fs-laser ablated SRRs did not show significant FEFs as shown in Figure 4-10b. However, two of these SRRs were cleaned using fs-laser ablation. These two SRRs showed the lowest breakdown voltage changes and also had high Weibull moduli. Our initial SEM analysis showed regions with many alumina–metal interfaces as well as some nanoscale protrusions. Laser induced periodic surface structures (LIPSS) have been reported to result from fs-laser ablation and this is likely what we have observed in our samples [89]. Therefore, although we have not explored the cause of this performance improvement in depth, we believe it may be related to the generation of laser-induced periodic structures and triple-point enhancements.

### 4.4 Conclusion

By studying a variety of resonators, we find that performance can depend heavily on fabrication method, surface chemistry, and SRR base material. In particular, we find that the breakdown voltage in dark conditions can vary by as much as a factor of ~2.5–3×. Significantly, when also considering that Q-factor can vary by a factor of 3, we find that careful choice of
material and fabrication method influences power requirements for breakdown by an order of magnitude. Furthermore, it is found that the interelectrode gap size for SRRs in the range ~10–50 µm is not a significant contributor to plasma breakdown performance in atmospheric pressure Ar.

By employing Weibull analysis, we find that the consistency of breakdown as well as the breakdown voltage in dark conditions compared to under DUV illumination can vary widely. The correlation between Weibull modulus and breakdown voltage suggests that field emission is contributing seed electrons to breakdown for SRRs with gap sizes up to about 40 µm. Resonators with FEFs are shown to have both lower Weibull moduli and lower breakdown voltages. The presence of features that promote a high Weibull modulus is critical — an SRR with such features will breakdown consistently at the same voltage and also offer better performance under dark conditions. Since a wide distribution of Weibull moduli and performances are given here, this work may act as a guide for others to assess the performance of microwave microplasma generators with small gap sizes. Future work will include the extension of this study to smaller gap sizes and the use of differing electrode materials, geometries, and fabrication methods.
Chapter 5

Conclusions and Future Work

5.1 Introduction

This chapter summarizes the work in the previous chapters and discusses design suggestions for resonant, microwave microplasma generators. In addition, throughout the work for this dissertation there were often many additional/alternate paths of research that presented themselves. This chapter also presents some preliminary results for such paths and discusses work that could be carried out moving forward.

5.2 Summary, Conclusions, and Design Suggestions

This dissertation starts with a look at a new kind of resonant, microwave microplasma generator that is composed completely of dielectric materials. A proof-of-concept was given for the device, but it was found that the power requirements were quite high. Further optimization through different coupling schemes, resonator sizes, materials, and the use of different modes could make such devices more viable in terms of power requirements. However, the bulk of the work here focuses on SRRs, which require much less power in the current method of testing, but this can only be stated with an awareness for the lack of optimization of the all-dielectric plasma generator.

Plasma generation with SRRs has been studied at both low to moderate pressures as well as at atmospheric pressure. This study of SRRs has been done using four materials (Ag, Au, Cu, and CuO), but with a focus on Au and Ag. Fabrication techniques included screen-printing, fs-
and ns-laser ablation, electroplating, and e-beam evaporation. Although surface chemistry played a role in the case of the plasma induced film on Ag SRRs, it has been found that the primary driver for differences in plasma ignition power at low-to-moderate pressures is Q-factor for Au and Ag SRRs. Q-factor was directly related to microwave conductivity and defects such as porosity contributed to a lowering of Q-factor, especially in Au SRRs. In contrast, at atmospheric pressure it was found that surface morphology and chemistry began to play a much greater role.

Plasma ignition performance at atmospheric pressure was quantified using the Weibull modulus and the associated characteristic breakdown voltages. A trend was found where high Weibull modulus corresponded to lower breakdown voltage in dark conditions. The differences in dark breakdown voltage could span approximately an order of magnitude when comparing SRRs with low and high Weibull modulus. It was hypothesized that the cause of this performance difference was related to field-emission which can be promoted by FEFs and can be inhibited by smooth electrode geometries and the presence of alumina. The surface morphology and chemistry were found to depend heavily on fabrication technique. Fabrication technique, in addition to changing performance through surface morphology and chemistry also independently modified Q-factor.

As a result of these studies it is possible to make a few recommendations for the design of SRR, microplasma generators. First, to allow for the highest possible Q-factor, it would be important to start with a dense, smooth film of a high conductivity material such as silver. To help reduce roughness of the film, which can contribute to conductivity losses, it could be important to use a smoother substrate than the ~1-µm root-mean-square roughness of the substrates used in this dissertation. One way to produce a high-density Ag film of uniform thickness would be to use E-beam evaporation. An issue that arose when E-beaming Cu SRRs was the use of a low-conductivity, Cr bond coat that was about 1µm thick. This bond coat likely reduced Q-factor of the Cu SRR. With further experimentation this thickness could likely be
reduced to the 10-100nm range. Furthermore, the E-beamed SRRs were deposited with a high deposition rate and no annealing, which could have led to more defects and smaller grain size, both of which can reduce conductivity. Although not explored in this dissertation, SRRs should be designed such that Q-factor and gap voltage can be optimized. For instance, resonators which are too thin can reduce Q-factor due to radiative and resistive losses, but SRRs which are too wide have a high capacitance and thus lower impedance leading to reduced gap voltage.

In addition, it was found that the fabrication technique could influence Q-factor by, for instance, producing smaller features, less inhomogeneity in thickness, and steeper side walls. Both fs- and ns- laser ablation were found to produce high Q SRRs relative to screen printing. In the case of Ag SRRs, the laser-ablation method did not appear to play a large role. However, fs-laser ablation did not melt the alumina substrate and was capable of producing FEFs that assisted in breakdown. Therefore fs-laser ablation would be recommended for producing high Q and also producing FEFs for higher consistency in breakdown and lower breakdown voltages in dark conditions. Other possibilities for gap fabrication are discussed in Section 5.4. Further benefit could be achieved by first coating the SRRs with a film such as alumina before fs-laser ablation. As discussed in Section 5.3, alumina can be useful for protecting the silver from degradation due to the plasma while also reducing breakdown voltage at lower pressures. Since features in the gap itself were associated with better performance at atmospheric pressure, the removal of the alumina in the gap with fs-laser ablation should be sufficient to allow for these benefits while also allowing protection of the top surface of the Ag SRR.

5.3 Dielectric Coatings for Plasma Generation at Reduced Power

During low pressure studies of SRRs it became evident, as discussed in Chapter 3, that the surface of the resonator influenced the breakdown power at low pressures. Although the film
previously studied showed a negative effect from the perspective of reducing breakdown power, it was hypothesized that other films may deliver more propitious results. Figure 5-1 shows the ignition power of Ag SRRs and Ag SRRs coated with ~1µm of alumina that was deposited via e-beam evaporation. The alumina-coated resonators show up to a ~30% reduction in power required for plasma generation at the lowest pressures. In addition, as shown in Figure 5-2, the alumina film prevents the formation of the dark film, which was discussed in Chapter 3, that reduces SRR performance. When considering that the dark film that builds on the resonator ultimately decreases performance, by up to ~20% on a previously studied resonator, the steady-state reduction in breakdown power for a coated vs. uncoated resonator can be as much as ~50%.

The mechanisms for this performance increase are not known, but it is possible that the alumina film is storing electrons from previous plasmas, which are subsequently used to help in the generation of the next plasma. This hypothesis is supported by the fact that the performance benefit of the alumina film is not seen unless a plasma has been generated recently (within a few minutes).

Figure 5-1: The ignition power vs. pressure of Ag SRRs on average and Ag SRRs with alumina coating.
In addition, it has been found that other insulating films (silicone oil and polyvinyl alcohol) can also reduce the power required for plasma generation. Exploration with a variety of dielectric films of varying permittivity and loss could help in determining the mechanisms for ignition power reduction. Higher permittivity materials may show a larger effect due to increased charge storage. For instance, classical electrostatics can give an approximation of the effect of permittivity on surface charge. The surface charge that accumulates on a dielectric half plane \((z \leq 0)\) as a result of a charge nearing the dielectric surface at \(z = 0\) is given by: [105]

\[
\sigma = -\frac{q}{2\pi} \frac{\varepsilon_d - \varepsilon_0}{\varepsilon_d + \varepsilon_0} \frac{d}{r^2 + d^2},
\]

(5-1)

where \(q\) is the elementary charge, \(d\) is the distance the charge is from the surface along the \(z\) axis, \(r\) is the radial distance from the \(z\)-axis, \(\varepsilon_d\) is the dielectric permittivity, and \(\varepsilon_0\) is the permittivity of free space. The surface charge, a function of the permittivity, can act as a potential well for charges approaching the dielectric surface. By increasing permittivity/surface charge, it may be possible to capture more charge and decrease breakdown voltage. Films with more loss could also allow more insight into the mechanism for reduced ignition power — they would likely store
charge for shorter amounts of time and thus the reduction in breakdown power would decrease — especially as a function of time. One route to increase loss for an oxide film would be to deposit it in a very low oxygen environment that would allow oxygen vacancies to form. Reduction in a hydrogen environment after deposition is another possibility to increase loss.

5.4 Focused-Ion Beam Fabrication and Field-Emission-Enhanced Breakdown

Laser ablation, while superior to screen-printing in terms of achievable resolution, is still limited to ~10-µm lines/spaces. An alternative to laser ablation that could potentially produce submicron electrode gaps is focused-ion beam (FIB) milling. FIB milling also can allow for the patterning of very fine geometry such as the scalloped gap SRR shown in Figure 5-3. The widest distance between the electrodes is ~10 µm and the narrow point-to-point distance is 2.4 ± 0.4 µm. This SRR stopped functioning after multiple tests in plasma. The resonator showed small changes after plasma generation with the exception of one area, which is highlighted in Figure 5-3. The sharp edges appear rounded and energy dispersive x-ray spectroscopy shows an increased amount of aluminum, oxygen, and fluorine in this area. This resonator also showed a very low breakdown voltage (as low as 101 V in atmospheric pressure Ar and as low as 182 V in atmospheric pressure nitrogen). Breakdown voltages this low are unusual. For comparison, a resonator fabricated with a gap size of 2.6 ± 0.7 µm via FIB showed a breakdown voltage in Ar of ~150 V and ~280–330 V in nitrogen. It is believed that the very low breakdown voltage on the scalloped gap resonator may be as a result of field emission. This example suggests that resonators fabricated with new geometries allowed via the precision of FIB may be the key to achieving field-emission enhanced breakdown at very low powers. Unfortunately, at least currently the reliability of the device appears to be low, which may be attributable to the damage at the particular site shown in Figure 5-3. An additional difficulty moving forward is that FIB fabrication often deposits Ga on the
surface of the resonator. Preliminary results suggest that the Ga can short the resonator gap and its effects on plasma ignition are also not understood.

Figure 5-3: Au SRR with scalloped geometry fabricated using FIB shown (left) before and (right) after plasma generation in atmospheric pressure nitrogen. The insets show a close up of an area of the resonator which was damaged during plasma generation.

5.5 Atmospheric Pressure Breakdown in Nitrogen

Nitrogen, more so than Ar, becomes interesting when attempting to induce field emission since the electric fields require for breakdown are higher. Currently, several resonators fabricated using FIB are being studied in both Ar and nitrogen as shown in Figure 5-4. Again, no clear trend is seen with regard to gap size and breakdown in Ar, a result that was seen previously but is now extended down to gap sizes of ~2 µm. All resonators show almost the same performance whether in UV or dark — according to the evidence put forth in Chapter 4, this is the result of small-scale field emission producing seed electrons.
The resonator labeled R1 is the same resonator shown in Figure 5-3. The characteristic breakdown of R1, while higher than the minimum it achieved, is still much lower than the other resonators. In argon, R1 did not show an exceptional characteristic breakdown. Another interesting feature of these resonators in nitrogen is that it appears that the Weibull moduli are higher than in Ar. Currently, it is speculated that this may be due to a variety of factors including damage to the resonator from nitrogen plasma, interactions of nitrogen plasma and gallium, and low-energy electron losses to vibrational modes in nitrogen.

Figure 5-4: Gap size vs. breakdown voltage for Au SRRs with gaps fabricated using FIB in Ar and N₂.
References


Appendix

Non-Technical Abstract

With the advent of microplasmas, what was once considered impossible, the generation of stable, low-temperature plasmas at atmospheric pressure was demonstrated in lab. Such microplasmas have since found applications in diverse fields including nanomaterial synthesis, medicine, and metamaterials. One promising route to microplasma generation is through the use of microwaves since they have a tendency to be much less destructive than plasmas excited with lower frequencies. This dissertation focuses on the materials aspects of microwave microplasma generation. A proof-of-concept for a new microplasma generator, the all-dielectric, microwave, microplasma generator is introduced. One main advantage of such a device is the absence of reflective metal components, which may allow new possibilities for future plasma metamaterial designs. This work is followed by studies of ring resonators from low pressure to atmospheric pressure. Ring resonators of different materials that are fabricated using various methods including ultrafast-laser ablation are explored. It is found that the choice of material and fabrication type contribute to an order of magnitude difference in power required for plasma generation. In addition, evidence for field-emission-assisted, microwave microplasma breakdown is presented.
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