Determination of Etching Parameters for Pulsed XeF_2 Etching of Silicon Using Chamber Pressure Data

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A technique is presented for determination of the depletion of the etchant, etched depth, and instantaneous etch rate for Si etching with XeF_2 in a pulsed etching system in real time. The only experimental data required is the pressure data collected temporally. Coupling the pressure data with the knowledge of the chemical reactions allows for the determination of the etching parameters of interest. Using this technique it is revealed that pulsed etching processes are nonlinear, with the initial etch rate being the highest and monotonically decreasing as the etchant is being depleted. With an initial pressure of 565 mTorr of XeF_2 an instantaneous etch rate of 4.1 μm/min in Si was recorded; for an initial pressure of 2.23 Torr an instantaneous etch rate of 9.18 μm/min was recorded. Additionally, the same data is used to determine the rate constant for the reaction of XeF_2 with Si; the reaction is determined to be second order in nature. Using the technique introduced in this paper the effect of varying the exposed surface area of Si is shown as well as the effect that pressure has on the instantaneous etch rate as a function of time. As a proof of concept an AlN resonator is released using pulsed XeF_2 pulses to remove a sacrificial poly-Si layer.

I. INTRODUCTION

Dry etching of Si with XeF_2 has been widely employed due to its ability to isotropically etch Si without the damaging effects of liquid etchants or plasmas. Due to

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its simplicity and excellent selectivity, wet etches were initially chosen for etching of Si and poly-Si. However, when these etchants were first utilized, device features were relatively large and attached to a rigid substrate and therefore surface tension had no detrimental effects on device yield. However, as feature sizes shrank and the need for freestanding devices evolved, surface tension began to have deleterious effects on device yields. Dry etching with plasmas solved many of the problems that liquid etchants had due to alleviation of the surface tension issue. However, plasmas inherently contain ions, which are typically accelerated into the surface of the device and implant. As the size of devices increasingly shrink to the nanoscale, implantation of these ions begin to impair their function; ion implantation results in residual stresses and impaired electrical operation.[1] In order to avoid these previously stated issues caused by wet etchants and plasmas, XeF_2 is increasingly employed as a dry-chemical (plasmaless) etchant capable of isotropically etching Si. Interestingly, XeF_2 was initially proposed as an etchant of Si in the late 1970's.[1,2] However it was abandoned because of the advances in plasma chemistry. Seemingly it has re-emerged because of its uses to release large surface area MEMS and even more delicate nanostructures.[3–12]

XeF_2 in its vapor phase spontaneously etches Si at a rate as high as 10 μm/min, at room temperature.[13] Sublimation of the solid phase XeF_2 occurs at 3.8 Torr.[14] Thus a vacuum system capable of achieving pressures only in the medium vacuum range is required for sublimation. The primary chemical reaction of XeF_2 with Si is given in Eq. (1):[5,15,16]

$$2XeF_{2(g)} + Si_{(s)} \rightarrow SiF_{4(g)} + 2Xe_{(g)} \qquad (1)$$

There are two configurations of etching systems in which XeF_2 is commonly employed: a continuous etching system and a pulsed etching system. In the continuous etching system an open-volume etching system is utilized wherein a constant flow of XeF_2 is allowed to pass over the sample. This configuration was more commonly found when XeF_2 was initially conceived of for the etching of Si, particularly in the late 70's and 80's.[1,2,15] In more recent times, XeF_2 is more commonly found in a pulsed etching configuration, wherein a pulse of XeF_2 is allowed into a closed-volume etching chamber.[17–19] This method is commonly preferred because XeF_2 is typically used to remove sacrificial layers of Si where the etch rate need not be constant or controlled. Additionally, the requirements of the equipment for the etching chamber are relaxed considerably.

In Eq. 1, the number of moles of gas before the reaction and after the reaction changes from 2 to 3. If etching occurs in a fixed volume etching system, this will increase the number of moles present in the system, and will result in an increase in pressure eventually leading to an overall 50% increase in pressure of the entire system. Thus in a pulsed etching system by simply measuring the pressure change of the system, correlations can be made between pressure and the depletion of the etchant, etched depth, instantaneous etch rate and other factors tied to these values. Using the technique described herein, better process control can be attained with XeF_2 etching of Si. Note that this phenomenon can be exploited in any reaction occurring in a fixed volume where the number of moles either increases or decreases after undergoing a chemical reaction. Serendipitously, this is the experimental for determination of rate constants for chemical reactions as well.

In this study, the depletion of etchant, etched depth and the instantaneous etch rate of Si will be determined in a vapor phase etching system operating in a pulsed mode of operation. Monitoring of the pressure results in real-time monitoring of the depletion of etchant, i.e. complete reaction of the etchant. Etchant depletion is determined by monitoring the pressure of the system and waiting for it to reach its asymptotic value. The etched depth (μm) and the instantaneous etch rate (μm/min) are determined from the same pressure data when the exposed area (unmasked) of Si is known and correlated to the number of Si atoms (monolayers) removed for a given pressure increase. This data indicates that XeF2 etching with Si is initially reaction rate dependent and transitions to a transport limited condition. Additionally, it is also demonstrated that the rate constant for the reaction of XeF_2 with Si can be found using the same pressure data and coupling it with knowledge of the chemical reactions involved. Section II describes the experimental setup and methodology, Section III describes the results and method of their analysis, and in Section IV further validation and utility of this method is explored.

II. EXPERIMENTAL SET UP AND METHODOLOGY

A custom-built pulsed etching system was utilized in this work. The system consists of three main chambers: source, expansion, and etching chambers. XeF_2 is moved through theses chambers serially to etch Si.

The following is a synopsis of the procedure utilized during an etching sequence; a more detailed description is available in Ref. [20]. XeF_2 is loaded into the source chamber. Air present in the source chamber is then evacuated. Note that evacuation in all cases, in this work, refers to using a scroll pump that evacuates all chambers to approximately 10 mTorr. The evacuated expansion chamber is then opened to the source chamber allowing the XeF_2 to sublimate or 'expand' into it. Once a desired charge pressure is achieved, 1 Torr in this study, the expansion chamber is again isolated from the source chamber. The charge is then released into the etching chamber, with a volume of 14.13L, and the pressure between the two chambers is allowed to equilibrate at 565 mTorr of XeF_2 at which time the etching chamber is isolated from the expansion chamber. Pressure equilibration occurs in less than 300 msec in the system. Etching then takes place over a set period of time. This process is commonly repeated (looped) many times in order to remove the amount of Si desired. For most experiments, the pressure is monitored for a period of 500 sec. in order to ensure that all etchant is depleted.

In this work, it is demonstrated that monitoring of the pressure in the etching system allows for the determination of the complete depletion of the etchant, etched depth, instantaneous etch rate, and the rate constant for XeF_2 etching of Si. This is possible because the etching chamber is a closed volume. Thus if a reaction between the etchant and target material either increases or decreases the number of moles present in the gaseous phase, this will be reflected as a change in the pressure of the system. Note that this method cannot be utilized in common plasma-etching systems because the etching chamber is typically an open volume in which gases flow continuously and a constant pressure is attained by adjustment of flow rates and valves.

To determine the instantaneous etch rate, etch depth and complete depletion of the etchant only two pieces of information are needed: pressure data and the area of exposed Si for the sample. Pressure data in this work was recorded using an MKS Model PDR-C-2C and was sampled at a rate of 1 Hz. A leak check of the system was performed, and the leak rate was determined to be 6 mTorr/min. Thus over the period of etching, the pressure increase is approximately 50 mTorr which is less than 8% of the initial pressure (565 mTorr) of the etchant in the etching chamber. Reported data corrects for error due to leaks and residual gas. Exposed area of the Si is calculated from the actual dimensions of the mask and verified using a calibrated optical microscope.

Results for the final etched depth and instantaneous etch rate were verified with two independent techniques. The final etched depth was verified using a profilometer (Dektak 150) on the samples before and after etching. Comparison of the results from the new technique and profilometer results showed that results varied by no more than 3%. In order to verify the instantaneous etch rate another technique was need to make in-situ measurements. A Michelson Interferometer (Intellimetrics LEP400) was used through a window on the etching chamber to measure the real-time change in the depth of the etched Si. It was found that the interferometric technique and technique developed yielded etch rates that varied by 4% or less.

Real time analysis is possible with this technique. Pressure data is the only data collected during the etching, and all other parameters are known a priori. Thus an automated program can be written whose only input from the experiment is pressure data. All other information used to determine the complete depletion of the etchant, etched depth, instantaneous etch rate, and the rate constant for XeF_2 etching of Si can be specified before etching begins. In this work, pressure data was collected at 1 Hz, which allows for real time display of etching parameters. Pressure data can be collected faster to attain better granularity in the etching parameters. However it was unnecessary in these experiments whose duration was 500 sec.

Samples for this work were Si (100), patterned with SiO_2. SiO_2 has a selectivity of more than 1000:1 for Si etched in XeF_2.[2,15,21–25] The native oxide layer on the Si was removed using 10:1 HF for 10 seconds followed by a subsequent dehydration bake in an inert atmosphere for approximately 5 min.[26] Removal of the native oxide is necessary for etching to begin immediately due to the low etch rate of SiO_2 in XeF_2 (nearly 0 nm/min). The dehydration bake is performed to remove any adsorbed water, which can react with XeF_2 to form HF in the etching chamber. Exposed Si areas had critical dimensions greater than 200 μm. These areas were chosen such that loading effects[26] and amount of laterally etched Si are negligible. The XeF_2 used in this work was attained from SynQuest Lab. Inc. and was of 99.99% purity.

III. RESULTS

Referring to the reaction in Eq. (1), for every 2 moles of reactant (XeF_2) 3 moles of product (SiF_4 and 2Xe) will be created. From the ideal gas law,

$$PV = nRT \tag{2}$$

where P is pressure, V is the volume, n is the number of moles, R is gas constant and T is the temperature. Eq. (2) shows that increasing the number of moles present will proportionally increase the pressure in the system. For XeF_2 an increase of 50% is predicted by Eq. (1).

The change of pressure in the etching chamber due to etching of Si with XeF_2 is plotted in Figure 1. Again, the initial pressure of the etching chamber is 565 mTorr. In this experiment, Si is present in an amount greater than can be consumed by the XeF_2 released into the chamber. A period of 500 sec for etching was chosen such that all of the reactant could be depleted, leaving only byproducts in the system. Clearly the pressure in

Fig. 1 is approaching an asymptotic value. The final pressure was consistently less than the predicted 50% by approximately 4.7%. Averaging the results of 10 experiments attained this result; this average was found to have a standard deviation of 0.96%.

Lower than predicted measured values can be explained when considering the secondary reaction that occurs with the primary reaction (Eqn. 1). Houle (REF) concluded, using molecular beam mass-phase spectrometry, that Si_2F_6 is also a stable product that is formed by reacting XeF_2 with Si. The likely chemical pathway for this reaction is:

$$3XeF_2(g) + Si(s) \rightarrow Si_2F_6(g) + 3Xe(g) \qquad (3)$$

For this reaction 3 moles of the reactant creates 4 moles of product. This results in a 33% increase in the pressure. Moreover, it was shown that the fraction of each product is 85% SiF_4 and 15% Si_2F_6. Using these fractions for the byproducts, the predicted increase the pressure of the system is 46.5%. Again, the average value for this work was 45.3% +/- 0.96%. Thus the predicted value is nearly the same as the measured value when considering the experimental error. Differences between the measured and predicted values are expected because of the different conditions under which Houle performed his experiments versus the current experiments. Note that other researchers have also concluded that Si_2F_6 is likely a stable product of this reaction.

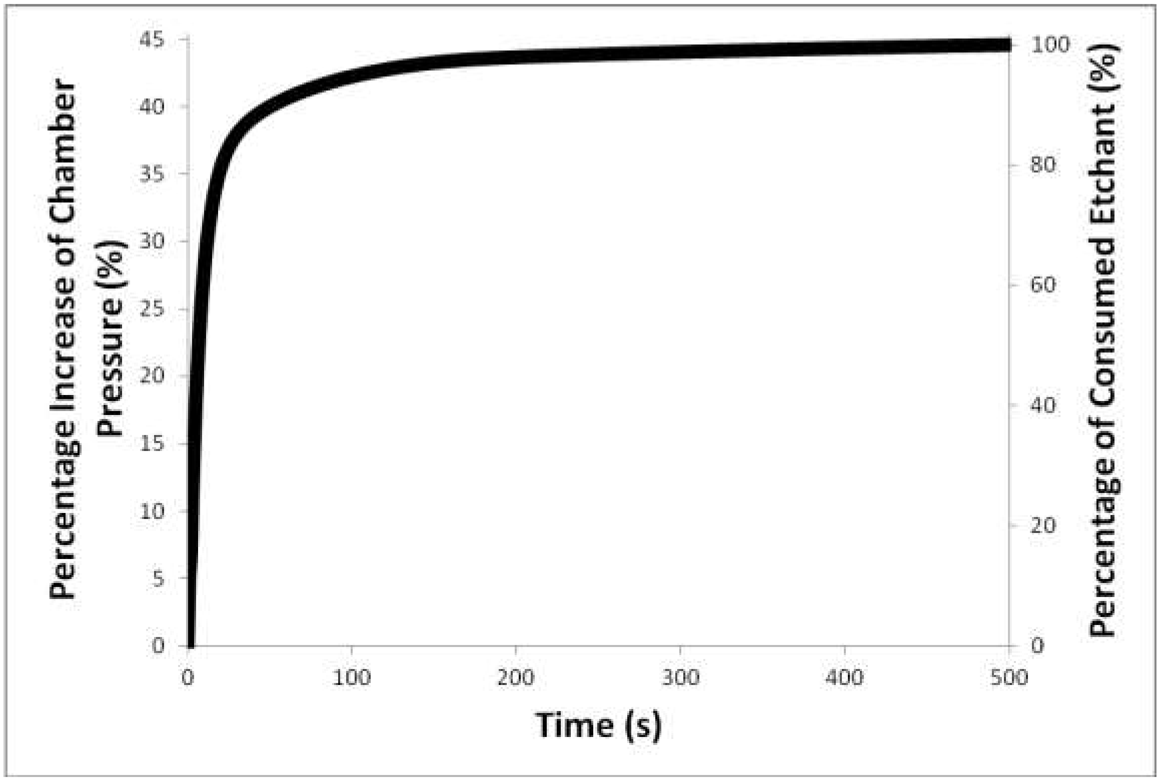

Figure 1: Percentage increase of chamber pressure as a function of time for etching of Si with XeF_2 in a fixed volume. Data indicates the pressure monotonically increases with time. A saturation pressure is eventually reached at ~144.6% of the initial pressure indicating that the reactant has been depleted. The final pressure is an indication that there has been a 44.6% increase in the number of moles of gas in the system.

From the pressure data in Figure 1, the instantaneous etch rate and etch depth can also be calculated. The etch depth is simply found by correlating the planar density of Si (6.78×10^{14} atoms/cm^2) with the increase in pressure. More specifically, the planar density multiplied by the exposed area of Si gives the number of atoms present at the surface that are available for etching. In this approximation, it is assumed that Si is removed one monolayer at a time. Next it is assumed that each mole of Si atoms on the surface that is etched, will lead to a 1.446 times increase in the number of moles in the gas phase, via Eqs. 1 and 3 as previously discussed. With this information, the depth of Si etched is plotted in Figure 2. By taking the numerical derivative of the etch depth with respect to time (finite difference approximation), the Instantaneous etch rate can be determined, Figure 2.

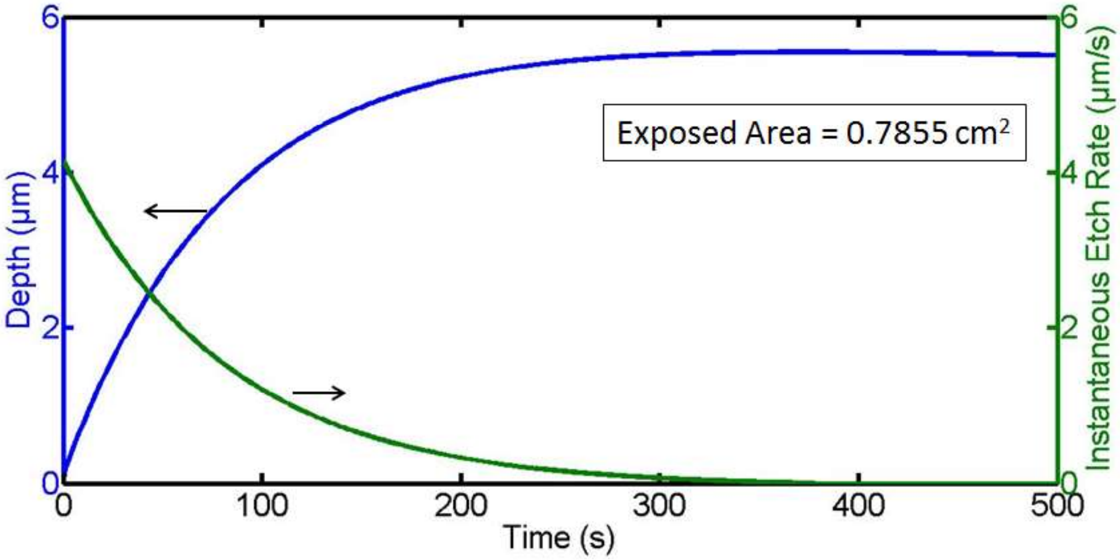

Figure 2: (Color Online) Etched depth and instantaneous etch rate as a function of time for XeF_2 etching of Si in a fixed volume. Etch depth is determined using the pressure data from Fig. 1 and information about the chemical reaction and material properties of Si. The instantaneous etch rate is determined by taking the numerical derivative of the etched depth with respect to time using the finite difference approximation.

Figure 2 offers interesting insight into the etching of Si with XeF_2 in a pulsed etching system. First the depth as a function of time is considered. A monotonic (not linear) increase in depth with time is seen to track the pressure's increase. This is expected due to its derivation from the pressure data and chemical reaction. Using this piece of information allows for control of the etched depth of a sample. The instantaneous etch rate for the sample is monotonically (not linearly) decreasing. Previous reports on the etch rate of Si using XeF_2 report only a single number.[13,15,17,19,24] This number appears to be an 'average' etch rate determined by dividing by etched depth by the duration of the etch.[13,15,17,30] Interpretation of the etch rate in this manner is misleading.

The etch rate is the result of complex set of surface reactions between the XeF_2 and Si and is not constant or linearly varying with time. To wit, the etch rate, under these specific set of conditions, varies from over 4.2 μm/min to nearly 0 μm/min in a nonlinear manner. This variation is due to a depletion of the etchant (XeF_2) and buildup of byproducts (SiF_4, Xe, and Si_2F_6) in the closed volume chamber. Previously, it was shown that the etch rate of XeF_2 with Si was limited by the incident flux of XeF_2 to the Si surface.[2] Clearly, decreasing the etchant concentration and increasing the byproducts over the surface will lower the incident flux of the XeF_2 and the etch rate will correspondingly lower.

Generally, surface reactions of F with Si consist of adsorption, dissociation, reaction, and desorption. The slowest process among these steps controls the etch rate. Reference ?? (Kojima91) goes into additional detail about this process. The main resistance to the reaction is the mass transport (diffusion) of F through an intermediate fluoride layer on the surface of the substrate. This effect is additionally slowed by the resistance of the diffusion of XeF_2 in the gas phase to the surface through the desorbed byproducts (SiF_4, Si_2F_6 and Xe). Thus the overall etching process is transport limited.

From a technological standpoint, the instantaneous etch rate data are useful as well. It allows one to determine when to stop an etch in order to optimize the speed of a process. For example, in order to minimize the total etch time one might run a system for a shorter period of time with multiple pulses versus a longer period of time with less pulses. Alternatively, one could maximize etchant use while minimize etching time. This could be accomplished by stopping the etch when the instantaneous etch rate is found to be approximately zero. This is the equivalent to looking for when the pressure increase of the chamber is approximately zero or, more exactly, equivalent to the leak rate.

The same pressure data also allows for determination of a rate constant for the reaction of XeF_2 with Si. Previously it was shown that the reaction pathways given by Eqn. (1) and Eqn. (3) describe the manner with which XeF_2 reacts with Si. These reactions occur on the silicon's solid surface and as such the rate constant found in this work is an 'apparent' rate constant due to it being a set of complex surface reactions and not purely reactions of the gas phase. Figure 3 shows that the inverse of the partial pressure of XeF_2 increases linearly with time for the first 30 sec. of the reaction; this period of time is assumed to contain reaction rate limited data. This type of dependence is typical for a second order rate reaction.[31]

$$-\frac{dP_{XeF_2}}{dt} = kP_{XeF_2}^2 \tag{4}$$

where P_{XeF2} is the pressure of the XeF_2 in the system as determined by the gas' stoichiometry analysis previously described and k is the apparent rate constant for the reactions occurring between XeF_2 and Si. The slope of the line in Fig. 3 corresponds to k and has a value of 0.308 $\text{mTorr}^{-1}\ \text{sec}^{-1}$.

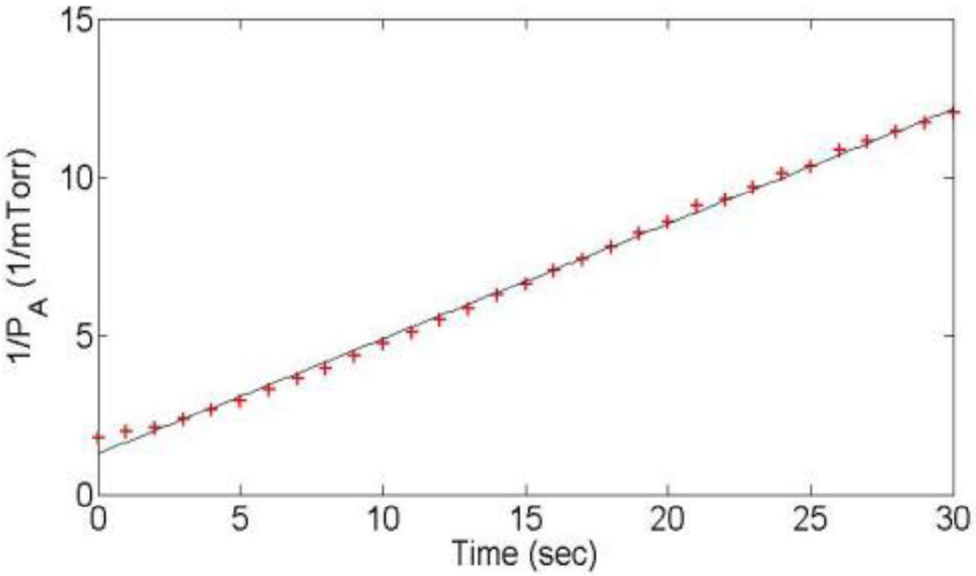

Figure 3: (Color Online) Plot of the 2nd order analysis plot as described in Eq. (4) for the first 30 seconds. Equation (4) describes the stoichiometry of XeF_2 undergoing both reaction described in Eq. (1) and Eq. (3). The slope is the apparent reaction rate constant (k) and has a value of 0.308 $mTorr^{-1}$ sec^{-1}.

IV. FURTHER VALIDATION AND UTILITY OF METHOD

Further studies are performed to validate and demonstrate the utility of the techniques previous described. The first study revolves around modifying the area of exposed Si available for etching.[5,19] Increasing the area of exposed Si increases the rate at which the Si is etched and thus increases the rate of pressure increase. A second study determines the volume of Si removed and the volumetric etch rate at varying pressures. Examining the volume of material removed and volumetric etch rate is useful when releasing suspended devices.[4–7] In the final study a suspended AlN resonator is released.

Figure 4 demonstrates how the pressure change in the chamber is affected by the amount of exposed Si directly. The leftmost curve is for an area of exposed Si equivalent to 78.5 cm^2. The rightmost curve is for an exposed are of 0.786 cm^2. Note that the rate of pressure increase for the sample with a larger exposed area of Si is significantly faster than that of the smaller exposed area. Larger exposed surfaces areas allow for an increased number of surface reactions. Furthermore, note that both curves asymptotically go to 45.3% as did the data presented in Fig. 1.

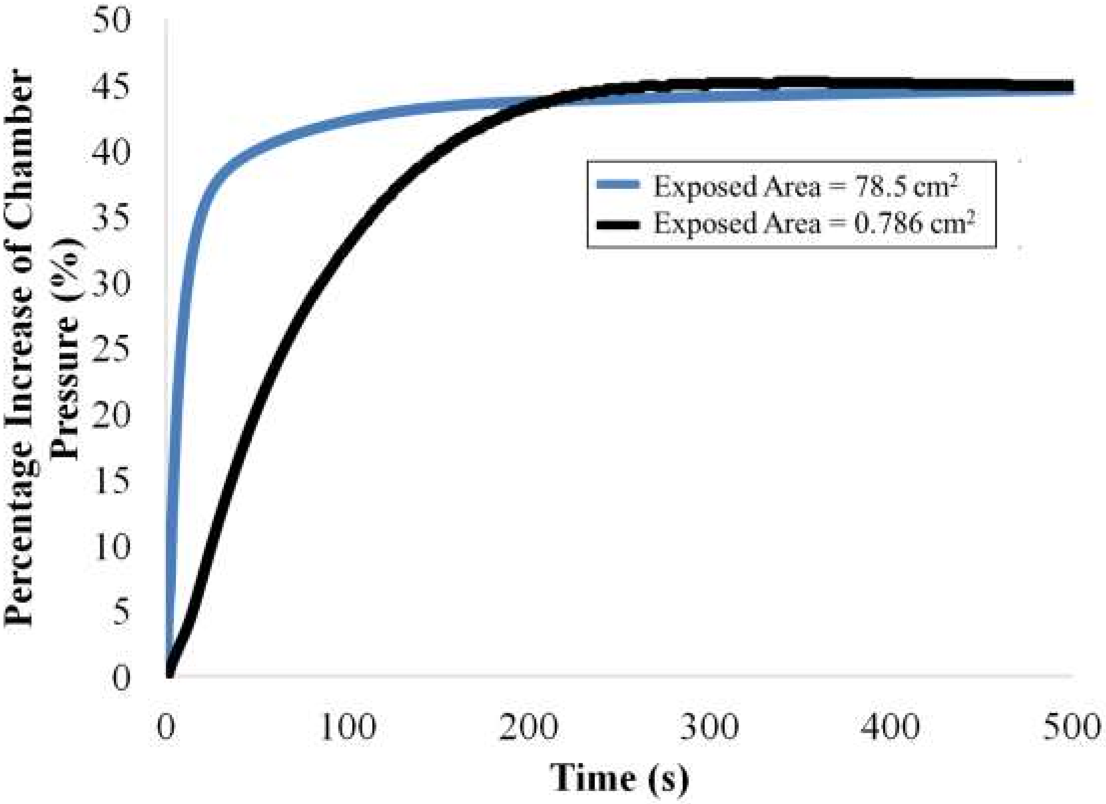

Figure 4: (Color Online) Percentage increase of chamber pressure as a function of time for instantaneous etching of Si with XeF_2 in a fixed volume. Data is presented for two different exposed surface areas of Si. The curve with the higher initial rate is for a larger surface area (78.5 cm^2) and the curve with lower initial rate is for a smaller surface area (0.786 cm^2). In both cases, the data indicates a monotonically increasing value of pressure that saturates with time. The saturation pressures are 144.6% of the initial pressure indicating that the reactant has been depleted and that there has been a 44.6% increase in the number of moles of gas in the system.

Again, using the exposed surface area allows for determination of the etch depth and instantaneous etch rate, see Fig. 5. The two sets of curves correspond to exposed surface areas of 1.57 and 0.786 cm^2. Increasing the amount of exposed surface area causes the etched depth to reach its maximum values over a shorter period of time. The maximum value of etched depth attained decreases for an increase in exposed surface area, but maintains a constant ratio between the exposed area and etched depth, i.e. the same volume of Si is removed. Instantaneous etch rate curves shift to lower values for larger values of exposed areas of Si. This indicates that the establishment and completion of etching has occurred over a shorter period of time.

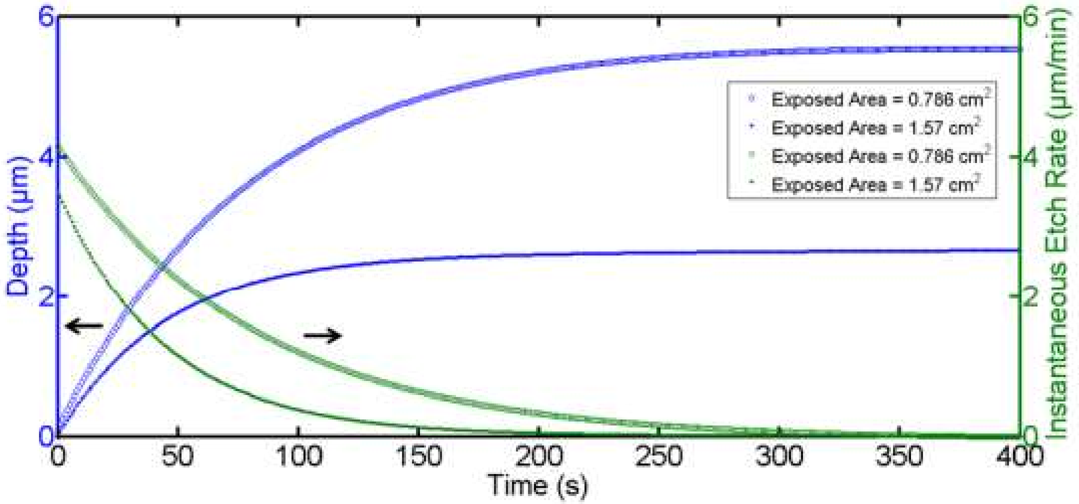

Figure 5: (Color Online) Etched depth and Instantaneous etch rate as a function of time for XeF_2 etching of Si in a fixed-volume chamber. Data is presented for two samples each with a different exposed surface area of Si. The larger the value of exposed Si surface area the lower the etched depth and the lower the instantaneous etch rate. Etch depth is determined using the pressure data from during etching and information about the chemical reaction and material properties of Si. The instantaneous etch rate is determined by taking the numerical derivative of the instantaneous etched depth with respect to time using the finite difference approximation.

In the second study an area of exposed Si (1.57 cm^2) is etched using differing pressures of XeF_2. Due to the varying initial pressure different volumes of Si are removed at different rates, see Fig. 6. Sets of curves such as those in Fig. 6a allow for easy identification of when devices sitting on sacrificial layers of Si are released. Often varying volumes of sacrificial Si need to be removed in order to release freestanding micro or nanostructures. Determining the volume of Si removed in these cases is usually not as easy as observing that a depth of Si has been removed from around the device and multiplying by the exposed silicon's surface area. Most micro/nanostructures have complex features and release holes under and around each of which a varying amount of Si is removed due to trenching and loading effects.[26] Though the data taken is taken for a large area of exposed Si that does not have trenching or loading effects it is still useful for gaging the maximum volumetric etch rate attainable.

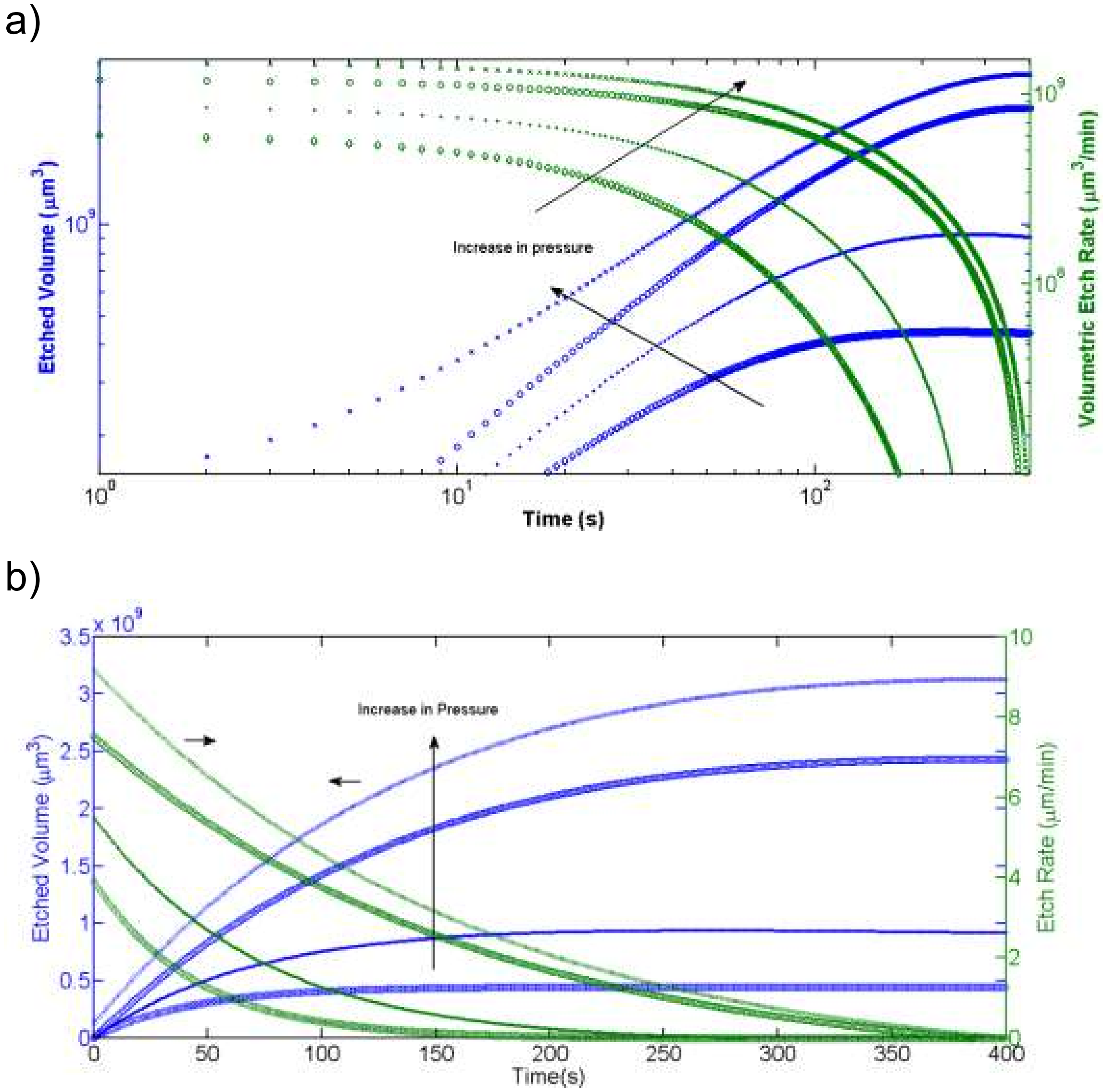

Figure 6: (Color Online) Instantaneous Etch rates for an exposed Si area of 1.57cm^2 for initial expansion chamber pressures of 1, 2, 3, and 3.8 Torr which correspond to the initial etching chamber pressures of 0.63, 1.2, 1,72, 2.23 Torr. Arrows indicate the direction of increasing pressure. a) Etched volume and volumetric etch rate as a function of time and b) (Linear) etch rate as a function of time.

Figure 6 also gives information about the instantaneous etch rate as a function of pressure. Increasing the pressure in the etching system will typically lead to higher instantaneous etch rates, which is typically desirable in many applications. For example going from 630 mTorr to 2.23 Torr increases the initial instantaneous etch rate from 3.92μm/min to 9.18 μm/min (Fig. 6b). However, too high of an instantaneous etch rate may lead to inadvertent and detrimental heating of the micro/nanostructures because XeF_2 etching of Si is an exothermic reaction.[32,33] The data shown in Fig. 7 shows a monotonic trend with increasing pressure that eventually saturates. Sugano et al.[24] observed a linear trend with increased charge (expansion chamber) pressure. However, their data only reached an etching chamber pressure of 233 mTorr. Data in Fig. 7 also shows an approximately linear trend for this pressure range as well. Fig. 7 also reaches much higher pressures and demonstrates that etching at elevated pressures, above approximately 2 Torr, does not dramatically increase the etch rate. Saturation of the etch rate with increasing pressure suggests a further resistance to transport over the surface of the samples, i.e. the flux of reactants into and products from etched surfaces are competing with one another. For identical samples this trend should hold regardless of the layout of the exposed Si until the point where feature sizes are on the order of the mean free path of the gas particles. Around this dimension transport in and out of the etch zone will be impeded and etching will considerably slower.

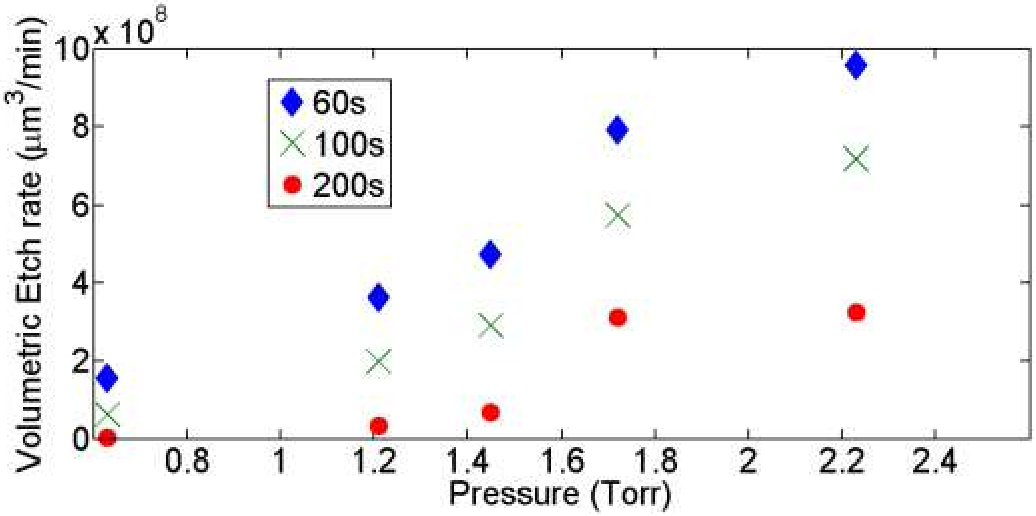

Figure 7: Volumetric etch rate as a function of etching chamber pressure at different time of etch period (60s, 100s, 200s) for XeF_2 etching of Si. Data is presented for an exposed area of $1.57 cm^2$. It shows a repeatable trend of volumetric etch rate of Si with XeF_2 with respect to the initial pressure of the etching chamber for every particular etch period.

In the final study an AlN resonator is released using pulses of XeF_2 to remove a sacrificial poly-Si layer. Fig. 8 is an image of a released device. The active layer is AlN, a piezoelectric material, with patterned Al electrodes. AlN has been used previously in the literature as a resonator.[34–36] On either side of the electrodes are two rectangular etch pits. These pits gave access to the poly-Si release layer that had previously resided beneath the resonator.

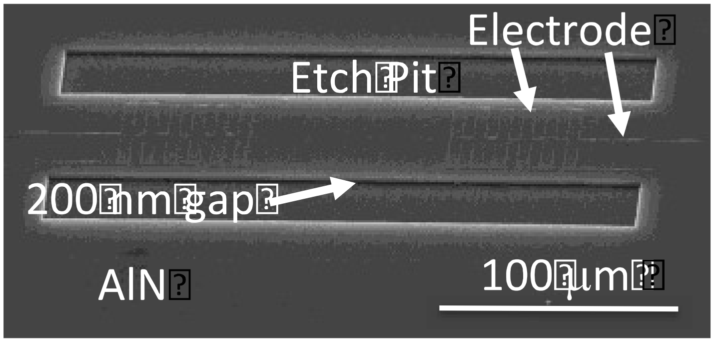

Fig. 8: Released AlN resonator

The poly-Si release layer has a well-defined volume as is schematically represented in Fig. 9a-b. A total volume of 8.03 x 10^4 μm^3 of poly-Si was used per AlN resonator for the sacrificial layer. The etch pit openings are 243 μm x 30 μm. 2.92 x 10^4 μm^3 of poly-Si is immediately available for vertical etching in the pit's opening. However an additional 5.11 x 10^4 of poly-Si is recessed under the AlN active layer. This poly-Si is laterally etched and as such etches at a lower rate than that which is immediately under the etch pit.

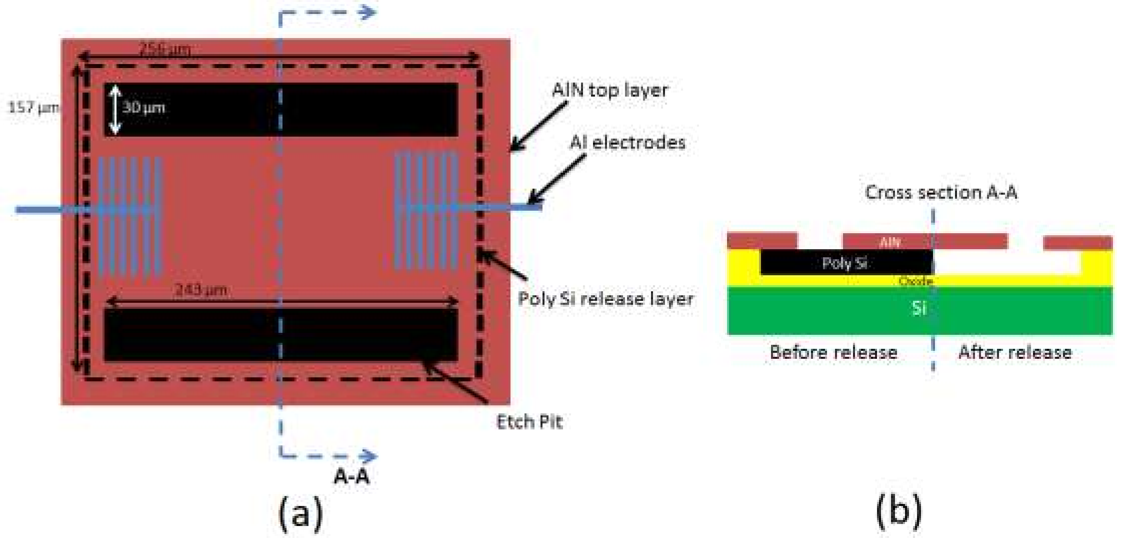

Fig. 9: Schematic of device to be released where (a) shows a top down view displaying the area of the poly-Si sacrificial layer and (b) a cross sectional view that gives layer thicknesses

Fig. 10 shows the amount of poly-Si that was etched for each of the 4 pulses used to release 16 AlN resonators simultaneously (all were on the same die) as well as the instantaneous etch rates for each pulse. Fig. 10a shows the volume etched for each pulse. The first three pulses etch the same volume of Si due to the availability of poly-Si to be etched. A final pulse is necessary to fully release the device, but the etched volume for Pulse 4 is less than the previous 3 because at a certain point the poly-Si to be etched runs out. The solid horizontal line, in Fig. 10a, demarcates the volume of poly-Si under all 16 resonators. A summation of the removed volumes (accumulated pulse) from all four pulses demonstrates that all poly-Si was removed. As verification that all poly-Si is removed a 5th pulse is attempted. The outcome was a no increase in pressure whatsoever indicating that all poly-Si was etched.

Fig. 10b shows the rate at which the poly-Si was etched for each pulse. Initial instantaneous etch rates decrease with increasing pulse number. This is due to the accessibility of the etchant to the poly-Si to be etched. Initially, the poly-Si in the etch pit opening is available to the etchant via a line-of-sight. After the first pulse this volume of poly-Si has been nearly all removed and the second pulse must then begin to laterally etch the poly-Si under the AlN active layer. The third pulse is only laterally etching the poly-Si from under the AlN. Finally, the fourth pulse is presumably removing the poly-Si in the furthest corners of the poly-Si release layers, which contains very little poly-Si and thus the etch stops without depleting all the etchant. In Fig. 10b the initial rates continually decrease for each pulse. At approximately 500 sec the instantaneous etch rates flip and the fastest instantaneous etch rate is for Pulse 3 and slowest for Pulse 1. At this time almost all the etchant has been depleted during Pulse 1 while for Pulse 3 a relatively large amount remains and thus can sustain a larger etch rate.

a)

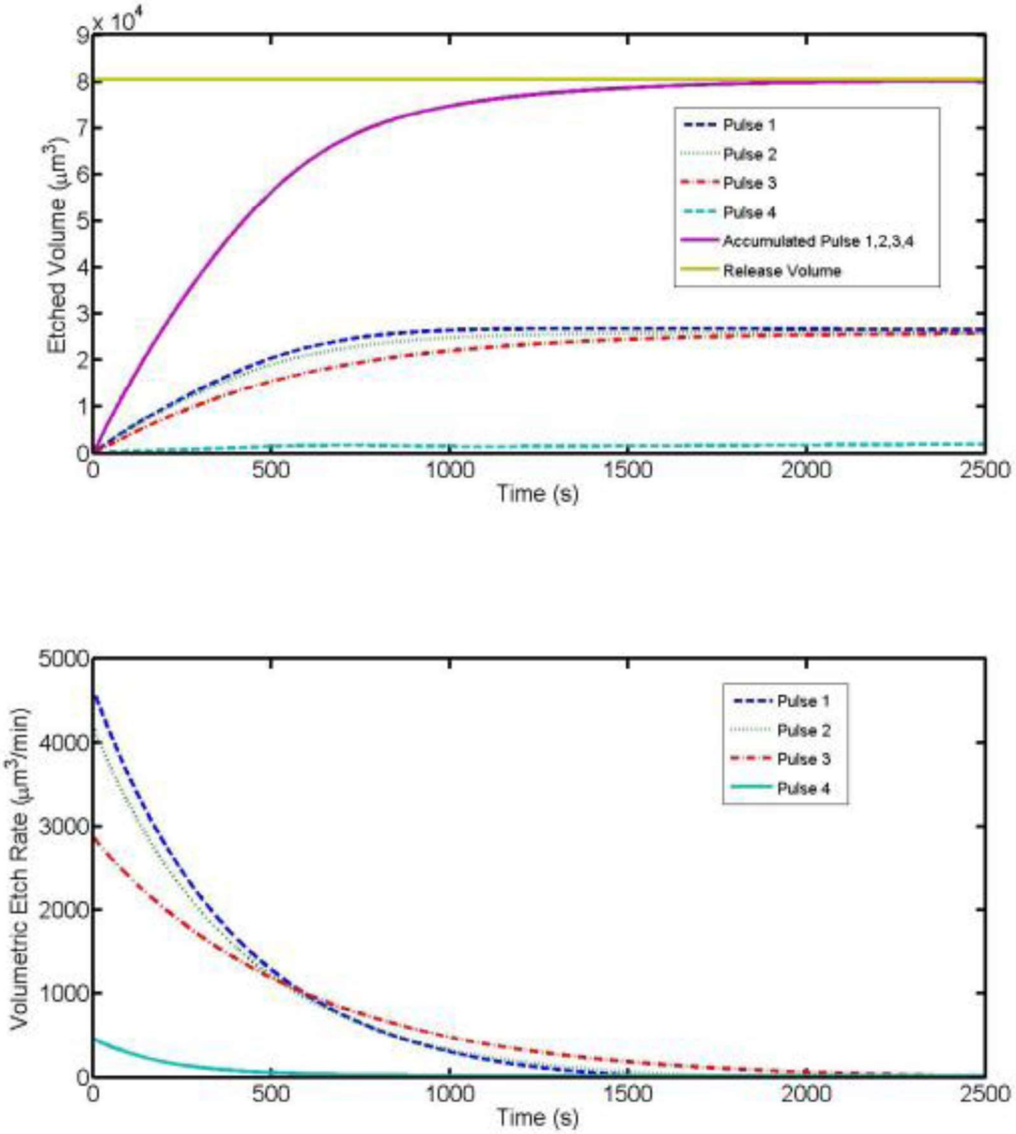
b)

Figure 10: (Color Online) Etched volume (a) and volumetric etch rate (b) as a function of time for XeF_2 etching of poly Si in a fixed-volume chamber. Data is presented for removing a sacrificial poly-Si layer under the AlN resonator shown in Fig. 8 with 4 pulses of XeF_2. Etched volume is determined using the pressure data from during etching and information about the chemical reaction and material properties of Si. The volumetric etch rate is determined by taking the numerical derivative of the volumetric etched depth with respect to time using the finite difference approximation.

V. SUMMARY

In this study, a simple technique has been presented for directly measuring: the depletion of etchant, etched depth, and instantaneous etch rate of Si etched by XeF_2 vapor with a pulsed etching system. This technique relied only on measuring the pressure of the etching chamber temporally and prior knowledge of the chemical reactions involved. It was shown that the pressure increased to 45.3% +/- 0.96% of its initial value, which was predicted by using to the two most favorable reaction pathways for XeF_2 etching of Si. Using the pressure data, exposed surface area, and planar density of Si atoms on the surface of the Si the etched depth was found. Taking the temporal derivative of the depth data yielded the instantaneous etch rate. A monotonic increase in the pressure corresponded to a monotonically decreasing instantaneous etch rate. Using an initial pressure of 565 mTorr, instantaneous etch rates higher than 4.1 μm/min were recorded and found to decrease noninearly with time. This was attributed to a decreased incident flux of XeF_2 for the surrounding gas due to a depletion of etchant (XeF_2) and buildup of byproducts. From the stoichiometry of the gas, an apparent rate constant for the reaction of XeF_2 with Si was found. This reaction was determined to be a second-order reaction because the inverse of the partial pressure of XeF_2 varied linearly with time. The measured rate constant was found to be 0.308 $\text{mTorr}^{-1}\ \text{sec}^{-1}$.

Additional studies were conducted that showed the direct correlation between exposed surface area of Si and the depth etched and instantaneous etch rate and a study was performed on how etch rates vary with the initial pressure of the etchant. It was found that larger values of exposed Si surface area lead to lower depths etched and lower etch rates. Correlation of pressure to etched volumes of Si and volumetric etch rates was shown to be beneficial for releasing micro/nanostructures. Linear and volumetric etch rates increase monotonically with increasing initial pressure of the etchant. For example going from 630 mTorr to 2.23 Torr increases the initial etch rate from 3.92μm/min to

9.18 μm/min. Saturation of the etch rate with increasing pressure shows that reactions are transport limited, i.e. the flux of reactants into and products from etched surfaces are competing with one another.

Finally, a case study for releasing an AlN resonator was performed to demonstrate the technique for practical devices. Four pulses of XeF_2 were required to release the device. The etchant of the first 3 pulses was completed depleted. Accordingly, the volume of poly-Si removed was the same. A final pulse was required to remove the remaining poly-Si and it was shown that the volume of poly-Si removed for that step was less than the other two. A summation of the volumes removed from the three pulses showed that amount of poly-Si removed could be accurately predicted before fabrication of the device. The volumetric etch rates were also reported.

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