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Hydrogen plasma etching of silicon dioxide in a hollow cathode system

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ABSTRACT

Chemical etching of various materials has been observed when hydrogen plasmas are used in material processing. In the case of the deposition of diamond films the preferential etching of sp^2 bonded carbon is considered to be of fundamental importance. A few papers have been published which have indicated that etching by hydrogen ions is different to that by hydrogen atoms. In this paper we describe the etching of silicon dioxide by hydrogen which was plasma-activated in a molybdenum-lined RF hollow cathode. The etch rate was seen to be thermally activated but decreased with increasing plasma power. The addition of a few percentage of helium increased the etch rate. The application of a −50 V bias to the sample holder almost doubled the etch rate indicating the importance of ion bombardment for the chemical reaction. At high plasma powers and substrate temperatures in excess of 450 °C a thin molybdenum deposit was formed on the quartz samples.

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1. Introduction

In recent years improved lithographic techniques have allowed a reduction in feature size in photon and electron sensitive resists into a range where conventional liquid phase chemical etching is no longer a viable method for pattern transfer [1]. Additionally, plasma etching has several advantages over wet chemical etching: it is ultrahigh vacuum compatible, very suitable to patterned substrates and can effectively remove native oxides and organic contaminants at room temperature [2,3]. Gases containing the halogens and halogen compounds have been widely used for etching semiconductors, metals and insulators [4]; but while those gases have proven to be very effective for the task, hydrogen could be used as an alternative for some plasma etching processes [5]. In particular, atomic hydrogen could be useful when a selective etching is required, since it will not etch as wide a range of materials as the halogens. The rationale of hydrogen plasma etching is the following: a plasma can be used as an effective means of producing atomic hydrogen, which is very reactive. If the hydrogen atoms can then chemically react with the material exposed to the plasma to form volatile hydride compounds, then the material will be etched [5].

In the field of thin film diamond and diamond-like carbon synthesis, chemical etching by atomic hydrogen is a well documented phenomenon [6–8]. A number of groups have studied and reported the etch rate of graphite and diamond as a function of the sample temperature and hydrogen atom flux [9,10]. The significantly higher etch rate of graphite compared to diamond is considered to be an important part of the process of formation of diamond films [6]. However, various reports indicate that the etching process is complicated; the etch rate increases, as expected, with increasing temperature but above 800 °C the rate decreases, in addition the rate decreases with increasing flux of atomic hydrogen [10]. Similarly, it has been reported that the etch rate of graphite using hydrogen ions is noticeably greater than using hydrogen atoms and that etch rate of diamond by hydrogen ions depends on the crystal orientation with the 100 direction being the smallest [11,12]. From such results it has been concluded that even with the small mass of the hydrogen, ion bombardment enhanced chemical etching can occur. Even though the etch rate of diamond by atomic hydrogen is small such treatments have been reported to produce a notable change in the surface roughness and optical properties of diamond films [13].

Studies of the selective deposition of diamond films on silicon substrates containing a mask pattern of silicon dioxide and studies of the nucleation and growth of diamond films on silicon dioxide substrates resulted in some interesting observations [14,15]; at high temperatures hydrogen was seen to etch the SiO_2 forming etch pits which facilitated diamond nucleation. Chemical etching of silicon and SiO_2 has also been reported when high density plasmas are used, as in hydrogen plasma ion implantation, but in the early work only a few details were reported indicating that the etch rate increased with the applied pulse potential (ion energy) [16]. Somewhat more recently, hydrogen chemical etching of crystalline and a-Si has been studied in depth [17]. The results are somewhat similar to the case of carbon etching in that the etch rate of a-Si is considerable higher than that of crystalline Si and the roughness of the surface of the etched material is increased [18]. However, the etch rate decreases with increasing

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sample temperature but increases with the hydrogen flux [19–21]. In fact, this phenomenon has been used to deposit crystalline Si on a hot substrate by hydrogen etching of a cold Si target at atmospheric pressure [22]. The decrease in etch rate with increasing temperature is much stronger for a-Si and it has been proposed that this is due to hydrogen induced crystallization of the surface of the amorphous target [23]. This process is thermally activated and therefore at high temperatures the surface crystallization is sufficiently efficient to reduce the effective etch rate.

In this paper we report the dependence of the hydrogen chemical etch rate of crystalline SiO_2 (Quartz) as a function of the plasma power and sample temperature.

2. Experimental details

The hollow cathode apparatus used for the experiments has been described in detail before [24–26]. The hollow cathode of 1.45×10^{-2} m diameter and 5×10^{-2} m length is a water-cooled copper cylinder the interior of which was covered with a molybdenum sheet. The hydrogen gas entered the hollow cathode from the top through a series of small holes such that the plasma was not ignited in the tubing above the cathode. The system was connected to a 1 kW RF power supply and mounted on a water-cooled flange so that the generated plasma flows directly onto the substrates mounted on the heater, located 10^{-2} m below the open end of the cathode. The experimental conditions used in this study (pressure 13.3 Pa and gas flux 10 sccm) were based in previous experiences with the system [26] and chosen to obtain the lowest possible deposition rates; the molybdenum was selected as the material for the cathode for the same reasons (the sputtering yield of molybdenum for 500 eV hydrogen ions is estimated to be 0.002 [27]). The substrate temperature was determined by calibrating the heater voltage values, using a thermo-couple placed on top of a quartz substrate under the experimental conditions but without plasma. It is expected, based on previous experiences, that the plasma produced an additional heating of approximately 80 °C.

The sample exchange chamber pressure was measured using a convectron gauge, the high vacuum pressure in the principal deposition chamber was measured using an ion gauge, and during the etching the gas pressure was monitored using a baratron. The samples were high quality quartz plate from Meller Optics. Pieces of quartz, 1×1 cm^2, were mounted behind a stainless steel mask with a 5×10^{-3} m diameter hole so that the exposed area could be etched by the hydrogen plasma during 30 min for plasma using powers of 25, 50 and 100 W and substrate temperatures of 523, 643, 723 and 823 K. For the plasma power which gave the highest etching rate, 25 W, the experiment was repeated, as a function of temperature, using a gas mixture of hydrogen +5% helium.

The depth of the etch was determined for all the samples using a DEKTAK II stylus profilometer. The surface of some selected samples was analyzed using a JEOL (JSPM-4210) Atomic Force Microscope (AFM) in tapping mode. Proton induced X-ray emission (PIXE) and 700 keV alpha particle Rutherford backscattering (RBS) using the IBM geometry studies were performed using the external beam setup at the 3 MV 9SDH NEC Pelletron accelerator at the Instituto de Física, UNAM, in order to determine if there was deposition of molybdenum on the samples during the etch process.

3. Results

Fig. 1 shows the measured etch rates as a function of the substrate temperature for the different RF plasma powers used. The etch rates are relatively low (0.5–2.5 nm/min) and increase with the substrate temperature, similar to other reports found in the literature [5,16]. Somewhat surprisingly the obtained etch rates were inversely proportional to the RF power. A considerable increase in the etch rate was obtained by using hydrogen +5 % helium. A plot of the logarithm of the etch rates versus the inverse temperature (Fig. 2) shows a clear Arrhenius type thermally activated dependence of the etch process. The activation energy obtained from the fit (Table 1) gives values between 8.2 and 11.6 kJ/mol. The difference between the values obtained for H_2 or $H_2 \pm He$ approximately within the experimental error of 10%, indicates that more work is required to establish if this difference is significant.

The surface of the samples (Fig. 3), studied by AFM, showed a large difference between the zone exposed to the hydrogen plasma and the masked one. The RMS roughness of the quartz, in the 1.7×1.7 µm measured area, increased from ~1 nm to ~10 nm.

Experiments carried out at 150 W resulted in considerably reduced etch rates and at the highest temperature of 450 °C the sample had a dark deposit on the surface. PIXE and RBS studies, Fig. 4, were performed on this sample and showed that the film was molybdenum of a thickness of approximately 2.8 nm. However, PIXE spectra of the samples prepared at lower plasma powers and temperatures did not show any trace of molybdenum, the only detectable contaminant was copper but this was found in untreated samples and therefore it was not a result of the etching process.

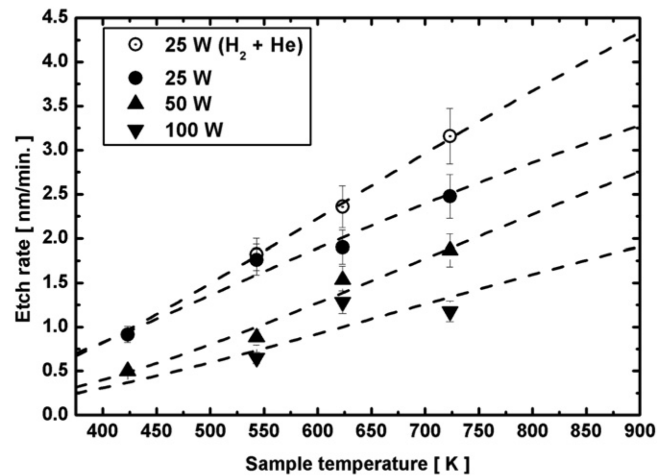


Fig. 1. The etch rate as a function of the sample temperature for the different RF powers used for both the hydrogen and hydrogen/helium gas mixture. The lines are a guide to the eye.

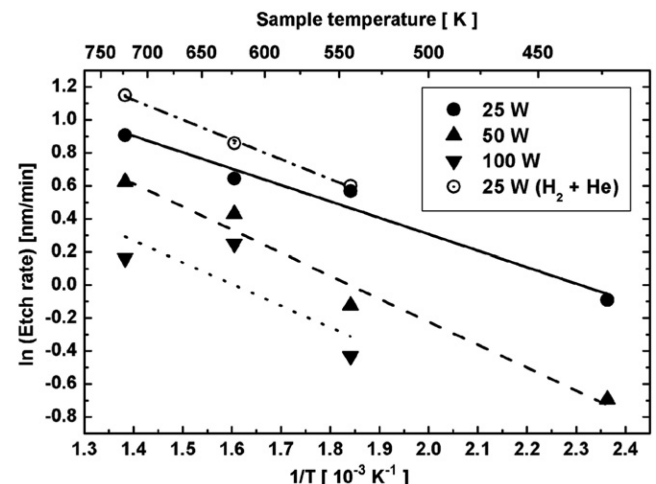


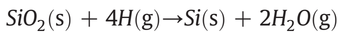
Fig. 2. Arrhenius plots of the logarithm of the SiO_2 etch rate as a function of the reciprocal of the temperature. The lines are the linear fit to the data which was used to calculate the values of the activation energy.

Table 1
The pre-exponential factor (A_0) and activation energy (E_a), obtained from the fit of the measured values of etch rates.

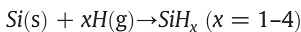
Plasma power [W]	25 (H_2 + He)	25	50	100
A_0 [nm/min]	16.4	9.9	13.0	8.2
E_a [kJ/mol]	10.0	8.2	11.6	10.9

4. Discussion

The chemical etching of quartz by atomic hydrogen must proceed via two chemical reactions



$$SiO_2(s) + 4H(g) \rightarrow Si(s) + 2H_2O(g)$$



$$Si(s) + xH(g) \rightarrow SiH_x \; (x = 1\text{–}4)$$

Although x can have values of 1 to 4, only the values 3 and 4 result in the formation of a volatile product, i.e. chemical etching. The silicon atoms that participate in the second equation are, probably, in the form of amorphous rather than crystalline state and, therefore, from the previously reported studies the etch rate might be expected to be greater than the rate we have observed [17,20]. Therefore, we propose that the first chemical reaction is the rate limiting process and from the increase in surface roughness the reactions probable occur at micro-defects in the surface of the quartz.

It is known that hollow cathode systems are capable of generating high density plasma $\geq 10^{16}$ m^3, and a degree of production of atomic hydrogen of $> 70\%$ [28,29]. Furthermore, it has been reported that the deposition rate by sputtering from a hollow cathode source increases with the plasma power and the gas flow rate [30]. Therefore, the use of a low gas flow and fairly low plasma powers should result in a high production rate of atomic hydrogen without deposition from the molybdenum target.

Both of the chemical reactions referred to above depend on the availability of atomic hydrogen and the production of atomic hydrogen in the hollow cathode should increase with increasing plasma power. Therefore, it was somewhat surprising to find that the etch rates decreased with increasing RF power.

L. Bardos et al. reported that the self-bias of a RF power hollow cathode depends on the applied power and that for small cathodes the bias can reach hundreds of volts [31]. We have carried out such measurements for our hollow cathode and find that the self-bias varies from −20 to −140 V as the RF power was increased from 20 to 150 W, see Fig. 5. We believe that the self-bias is part of the explanation of the reduction of the etch rate with increasing plasma power. The characteristics of the hollow cathode discharge means that a certain proportion of the hydrogen impinging on the quartz sample is ionized and from the work on carbon it is known that hydrogen ions are very efficient for etching. Therefore, we believe that the increased negative self-bias in the cathode, at high plasma powers, reduces the flux of hydrogen ions reaching the sample and this causes the reduction in the etch rate.

In an attempt to confirm the influence of the cathode self-bias voltage on the etch rate, the experiment at 723 K and 100 W was repeated, applying a substrate bias of −50 V to the sample holder and

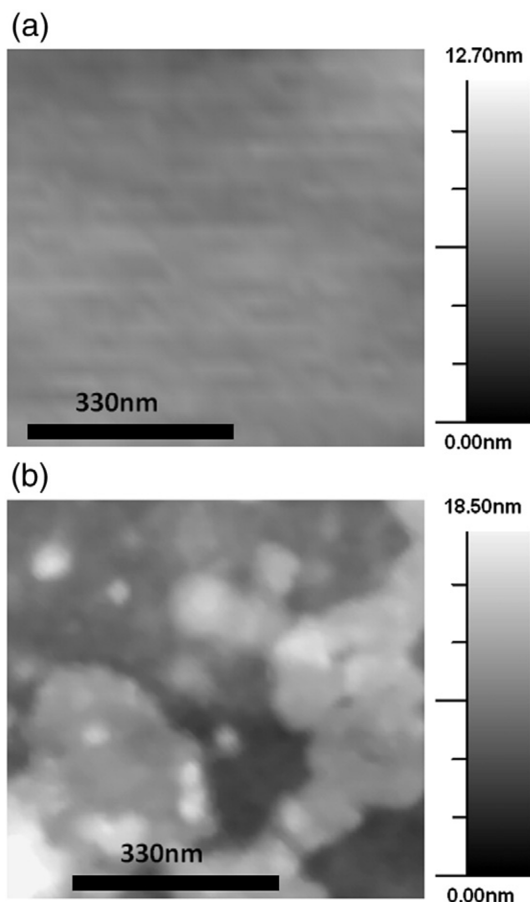


Fig. 3. A 2D AFM images of the SiO_2 surface before (a) and after (b) the hydrogen plasma etching.

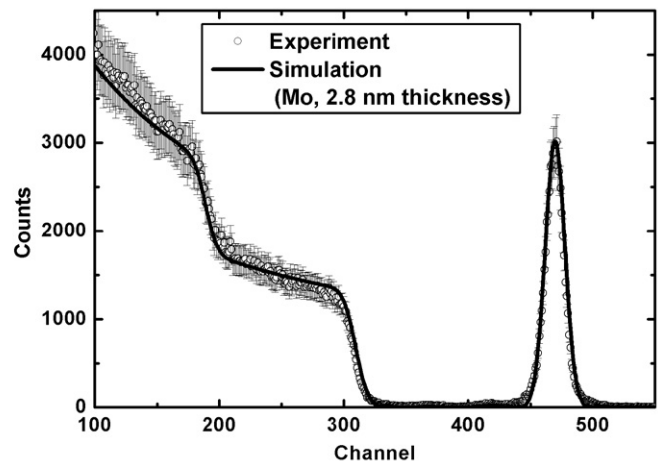


Fig. 4. RBS spectra of a sample etched at 150 W, showing the existence of a molybdenum film with a thickness of around 2.8 nm.

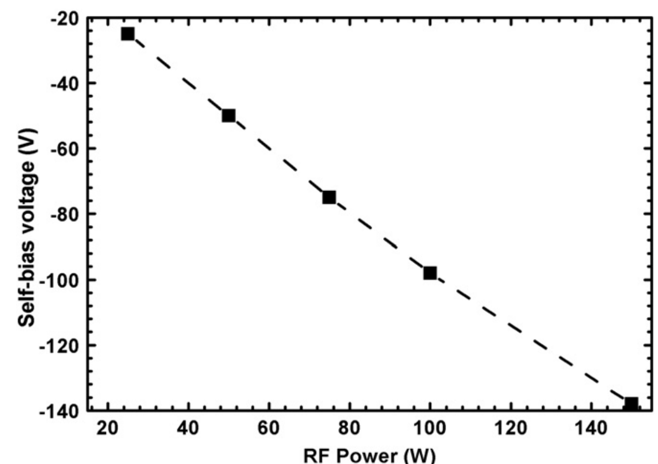


Fig. 5. The DC cathode bias as a function of the RF plasma power for the hydrogen gas flow and pressure used for the etch experiments.

mask; the etch rate obtained in this case was more than twice that produced without the substrate bias (~2.7 nm/min with substrate bias and 1.3 nm/min without substrate bias). We believe that this clearly demonstrates the importance of role of hydrogen ions in the etch process, although why they are a more efficient etchant is still not apparent.

The results shown in Fig. 2 clearly demonstrate that the dispersion in the etch rate data is larger for the higher plasma powers and that this is probably due to an increase in the surface roughness after etching. The uncertainty in the measurement of the etched depth in turn leads to the dispersion in the values of the activation energy.

Finally, the enhanced etching observed for the hydrogen/helium gas mixture may be due to a number of effects and requires additional work; the additional helium ions may enhance the ion bombardment, enhanced chemical etching or the formation of atomic hydrogen may be enhanced by resonant ionization phenomenon [32,33].

5. Conclusions

In this paper we have reported the use of hydrogen plasma in a hollow cathode system to etch a SiO_2 surface. We found that the etch rate is inversely proportional to the RF power and gave the possible cause of this behavior. It was also shown that by adding a small percent of helium to the hydrogen gas the process can be slightly enhanced. Although the obtained etch rates are small, they are enough to make hydrogen a viable candidate to halogens and their compounds when plasma etching of certain surfaces is required, especially if selective etching is required. This can be useful for several applications, for instances hydrogen etching could be used for transmission electron microscope sample preparation for metallic nanoparticles embedded in SiO_2, in replacement of the more commonly used ion milling which could cause damage to the nanoparticles.

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