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Oxidation Studies of Fluorine
Containing Diamond Films

by

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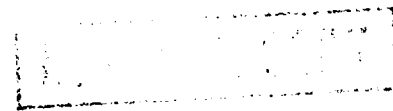
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The thermogravimetric method is used to study the oxidation properties of plasma grown diamond films both with and without fluorine. The oxidation experiments are carried out over a temperature range of $600^\circ C$ – $800^\circ C$ and in pure oxygen at one atmospheric pressure. Our experiments show diamond films with fluorine are more resistant (by as much as a factor of 4 at $700^\circ C$) to oxidation. The activation energy for oxidation, on the other hand, is at least a factor of 2.3 lower for diamond films with fluorine. These results lead us to postulate that oxidation mechanisms for diamond films are quite different depending on whether there is fluorine or not. For diamond films without fluorine the oxidation seems to proceed as a rate limited reaction, while for films with fluorine the oxidation seems to be a diffusion limited reaction. We have also found that there is a weak dependence of oxidation rates on film density, crystal texture, and the phase composition of the diamond film.

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Abstract

The thermogravimetric method is used to study the oxidation properties of plasma grown diamond films both with and without fluorine. The oxidation experiments are carried out over a temperature range of 600°C - 800°C and in pure oxygen at one atmospheric pressure. Our experiments show diamond films with fluorine are more resistant (by as much as a factor of 4 at 700°C) to oxidation. The activation energy for oxidation, on the other hand, is at least a factor of 2.3 lower for diamond films with fluorine. These results lead us to postulate that oxidation mechanisms for diamond films are quite different depending on whether there is fluorine or not. For diamond films without fluorine the oxidation seems to proceed as a rate limited reaction, while for films with fluorine the oxidation seems to be a diffusion limited reaction. We have also found that there is a weak dependence of oxidation rates on film density, crystal texture, and the phase composition of the diamond film.

The success in chemical vapor deposition of polycrystalline

diamond films has opened the way for potential application of these

films as protective coatings on a variety of substrate materials.

For example, it has recently been shown that diamond films on steel

surfaces can successfully resist corrosion [1]. Diamond films

have also been proven to be good optical coating materials which

can resist mechanical wear [2]. However, there are instances

where diamond films will be subjected to an oxygen containing

ambient at high temperatures. In such an environment it is noted that diamond will be readily oxidized (or vaporized) [3]. In fact, it has been shown that diamond oxidizes much more readily compared to graphite (which has a large fraction of its carbon atoms in double bond configuration) [4]. On the other hand, most chemical vapor deposited diamond films are composed of C - C or C - H bonds with average bond energies of 348 kJ/mol and 413 kJ/mol respectively [5]. It has also been shown recently that diamond films require more energy input to oxidize, compared to bulk diamond with comparable defect density [6]. Patterson et. al. have demonstrated that diamond powder (or grit), single crystal diamonds, as well as chemical vapor deposited (CVD) diamond films, can be fluorinated directly. By means of infrared and photon electron spectroscopy, they have shown that in most instances the fluorine is attached to the external surface. Once fluorinated, they find single crystal diamond slabs show enhanced resistance to further oxidation. In this article we study the oxidation resistance of diamond films which have incorporated fluorine during film nucleation and growth, and compare them with those that have not. What is the rationale for fluorinating diamond films to enhance oxidation resistance at high temperatures?

Recent experiments with slow positrons by Uedono et al and Sharma et al have shown that diamond films deposited with a microwave plasma can have defect densities as much as 0.4% and with void size of the order of 2 - 5Å [8]. Since etching process (in this case oxidation) propagates most readily along defects in

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crystals, it is important that we terminate as many dangling bonds as possible on the internal surfaces of the defect voids and the external surfaces of the diamond films. To enhance oxidation resistance, it is necessary to convert as many surface carbon - carbon bonds and carbon - hydrogen bonds as possible to some stronger carbon bonds.

The strength of the C - F bond is 485 kJ/mol and fluorine atoms are small enough to fit easily in the defect voids of the diamond films. Fluorine can be easily formed in a plasma, and by using CF_4 as a source we get both carbon and fluorine atoms for diamond film deposition. In the experiments reported here we have attempted to incorporate the amount of fluorine which is comparable to the defect (void) density of the diamond film. The rationale is to try to provide sufficient fluorine atoms to terminate a large fraction of dangling bonds of carbon atoms in the defect voids and on the surfaces. We anticipate such films with fluorine are more resistant to oxidation than films with internal and external surfaces covered mostly with hydrogen.

The experiments are performed in our microwave plasma deposition systems described elsewhere [9]. Typical deposition conditions are as follows: total gas flow rates between 100 and 200 sccm; gas composition 3%, 6%, 9% CF_4 or 1/2% CH_4 with a balance of 1/2% O_2 and H_2; total gas pressure 30 torr; microwave power 350-400W; substrate temperature 850°C-950°C. Silicon wafers, both (100) and (111) orientations are polished with 0.25 μm diamond powder and cut to 1 cm by 1 cm in size. A variety of films several microns

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thick are grown both with pure CH_4 and CF_4. The surface morphologies are examined with scanning electron microscope (SEM) and the carbon phase information of the film is obtained by Raman spectroscopy. From the Raman spectra, one can not differentiate between diamond films grown from CH_4 or CF_4. However, the SEM photos show a difference in surface morphology for diamond films grown at the same temperature. For example, films grown with CH_4 at 875°C show triangular faceted surface, while CF_4 grown films have continuous and rather smooth surfaces.

The amount of fluorine that has been incorporated in the diamond film is measured quantitatively to within a factor of 2, using secondary ion mass spectroscopy (SIMS) at the Charles Evans & Associates. All of the diamond films contain a few percent of hydrogen and a fraction of a percent of oxygen in addition to carbon. Films grown with CF_4 typically have on the average 10^{-19} cm^{-3} of fluorine distributed throughout the film.

After a diamond film is grown, the silicon substrate is removed in a solution of 3:3:5 $HF:HNO_3$: CH_3COOH etchant before performing the thermogravimetric analysis (TGA) experiment. The oxidation of diamond films takes place in a Perkin-Elmer TGA instrument which we have interfaced with a personal computer. Pure oxygen flows into the oxidation chamber at a rate of 40 sccm. The chamber is at atmospheric pressure. Data acquisition is done through the use of a customized program. Average values for both the weight and temperature are obtained each second for the duration of the oxidation experiment by measuring every 2ms for the

first 150ms of each second, and averaging those 75 values together. The typical diamond film sample weighs between 0.2 to 0.6 milligram, while the noise level of our detection is 1 bit (= 1.5×10^{-5} gram) for the 16 bit converter. In a typical oxidation experiment the temperature is manually ramped up to 700°C in approximately fifteen minutes and held at that temperature (700°C) for the duration of the diamond etching. From the weight loss curves, derivatives are taken to determine the etch rates as a function of time for various diamond growth conditions. Figure 1 shows etch rate plots of four different diamond films grown with different carbon gas sources and concentrations. The relative etch rates decrease, going from CH_4 to CF_4 sources with similar etch rates for 3% and 6% CF_4 concentrations. From these plots we note that diamond films formed from either 3% or 6% CF_4 gas source have etch rates about 1/4 of that of diamond films grown with 1/2% CH_4 gas source at about 700°C. (Note, we have compared etch rates of films with comparable Raman spectra.)

In figure 2 we plot the etch rates as a function of the oxidation temperature for graphite, diamond powder (1/4 μm in size from Mega Diamond), and plasma deposited diamond films of three different morphologies, using CH_4 gas source. We note the following etch behavior: for a given etch rate diamond powder (O) takes place at the lowest temperature, while graphite (◆) has the highest temperature, and the CH_4 grown diamond films have temperatures in between the first two. The slope for the faceted diamond film (X) is close to that of the diamond powder, while the

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cauliflower textured diamond film (▲) has a slope close to that of graphite. On the other hand, a CH_4 grown film (◇ , grown at a much slower rate or a more compact film) with very strong diamond Raman signal and a minimal detectable graphitic signal has a slope in between. The activation energy as measured from the plot for diamond powder is about 6.5 eV, while the activation energy for graphite is about 3.1 eV, and the activation energy of the CH_4 grown diamond films are between 4 eV and 4.7 eV. From these plots we see there is not much dependance of the etch rate on surface morphology of the films until the temperature is close to 700°C. At this temperature it is known that hydrogen atoms which passivate the diamond surfaces thermally desorb appreciably.

The etch rates as a function of temperature for diamond films grown with CF_4 gas source is plotted in figure 3. We note that the slops of these curves (or the activation energies) are about a factor of 2.3 lower than the films grown with CH_4 gas source. There does not seem to be any difference in the etch rate curves between that deposited with 3% (□) and 6% (♦) CF_4, neither is there an etch rate difference between films with different texture or morphology of the films. For instance, sample (□) is a faceted film while sample (O) is a non-faceted film grown with 3% CF_4 but different substrate temperatures. With 9% CF_4 as a source, the etch rate curve shifts slightly up but the shape is well preserved. Comparing CF_4 grown films with CH_4 grown films, we see that films grown from CH_4 (X) etch 4 times faster than CF_4 grown diamond films at about 700°C. But at lower temperatures, below 600°C, the CF_4

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grown films seem to etch faster.

We like to postulate an explanation to our experimental observation. In the case of diamond films without fluorine, we note the activation energy is around 4 eV, which is close to the energy value of single covalent bond of carbon. Thus, similar to the case of either oxidation of silicon or plasma etching of silicon, the oxidation (i.e. etching) of these diamond films is dominated by the surface reaction process. The etch rate is reaction limited. On the other hand, we believe that diamond films with fluorine have their surface covered with fluorine-carbon bonds (recent measurements by Freedman and Stinespring support this argument [10]) and, perhaps, a fraction of the internal interfaces as well. In the high temperature regime (around 700°C), the surface reaction with oxygen proceeds much slower, compared to the case when the surface is covered with hydrogen-carbon bonds (i.e. the case of diamond film with no fluorine). But as we have noted earlier, diamond films have a large percentage of defects and grain boundaries, so oxygen will diffuse readily into the internal boundaries and voids to etch the diamond film. Thus we believe for the case of fluorine containing diamond film, the reaction is diffusion limited and hence a lower activation energy (around 2 eV). This is possible because not all of the internal surfaces have fluorine bonds (but rather a large portion with hydrogen bonds or simple carbon-carbon bonds or dangling bonds). During oxidation at temperatures around 700°C, a larger fraction (comparing to fluorine) of the hydrogen will have been thermally

desorbed and reacted with oxygen, thus etching from within the film. At this point we do not have enough data to give a quantitative explanation of our observation.

In conclusion, we have shown that diamond films with fluorine etch much slower at high temperatures than diamond films without fluorine. We believe this is due to the termination of surface and a fraction of the internal surface (inside the defect voids) by fluorine atoms. The amount of fluorine incorporation is comparable to the density of defects as reported by slow positron measurements.

Acknowledgement

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Figure Caption

Figure 1. Relative etch rate plots for diamond films grown with three different concentrations of CF_4 and 1/2% CH_4.

Figure 2. Arrhenius plot for various forms of carbon: (♦) graphite; (▲) diamond film grown with 1/2% CH_4 with cauliflower surface texture; (◊) diamond film grown with 1/2% CH_4 densely packed crystalline surface; (X) diamond film grown with 1/2% CH_4 with well

faceted surface; (O) 0.25 μm diamond powder.

Figure 3. Arrhenius plot for a variety of diamond films: ($\square$) is a faceted film grown with 3% CF_4; (O) is a non-faceted film grown with 3% CF_4; ($\bullet$) is a film grown with 6% CF_4; (+) is a film grown with 9% CF_4; and (X) is a film grown with 1/2% CH_4.

Relative Etch Rate

Time (sec.)

3% CF4

6% CF4

9% CF4

1/2% CH4
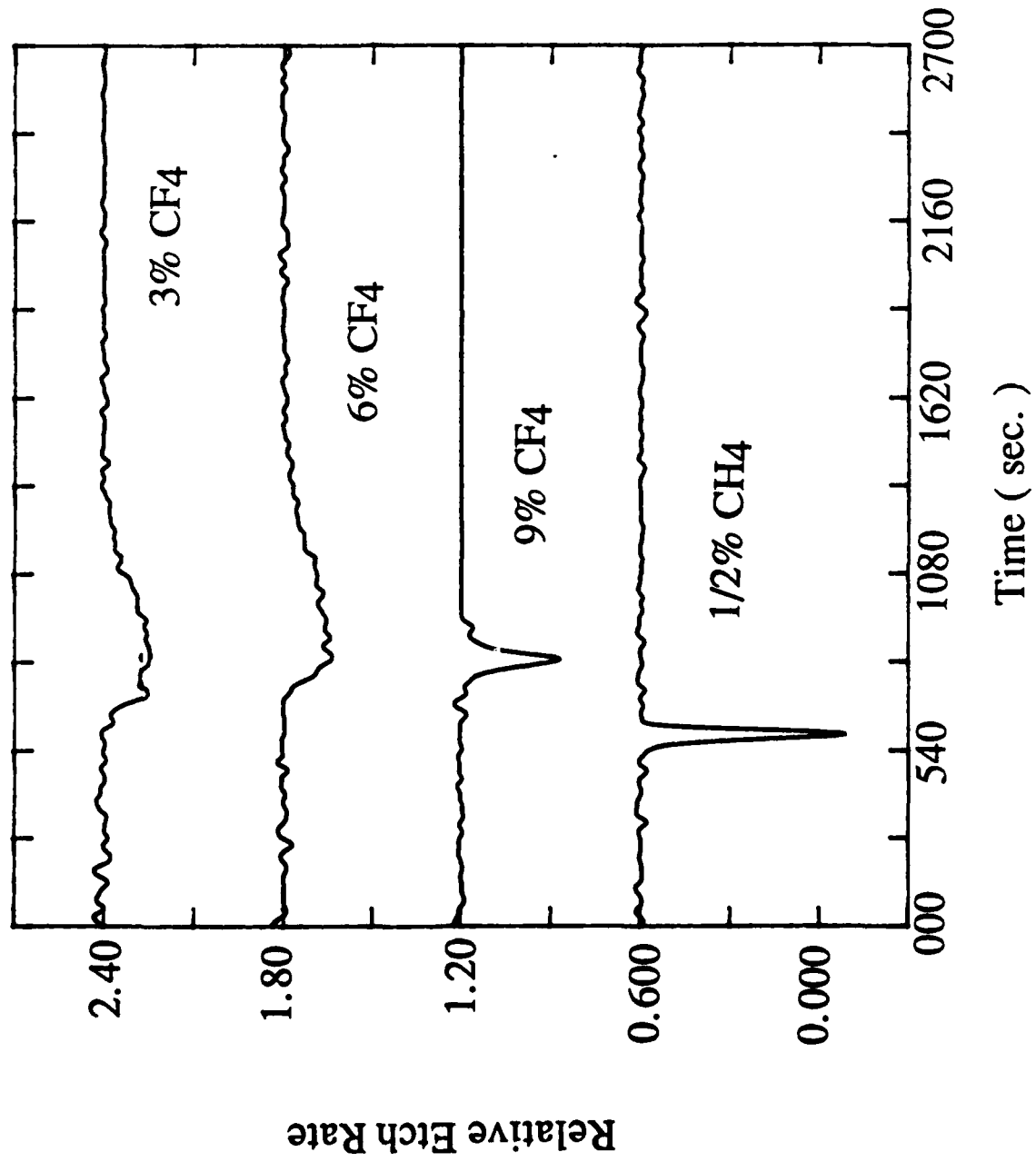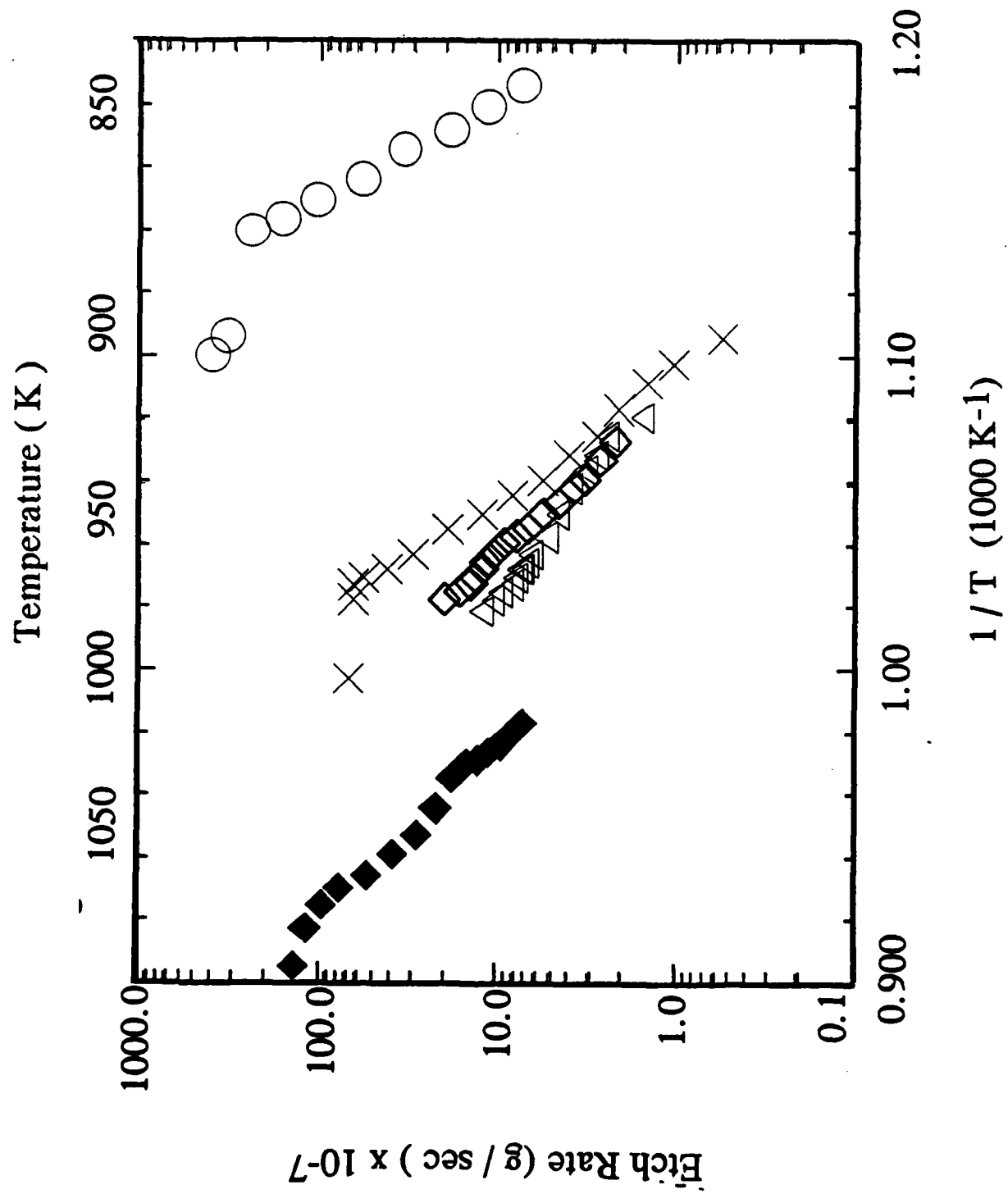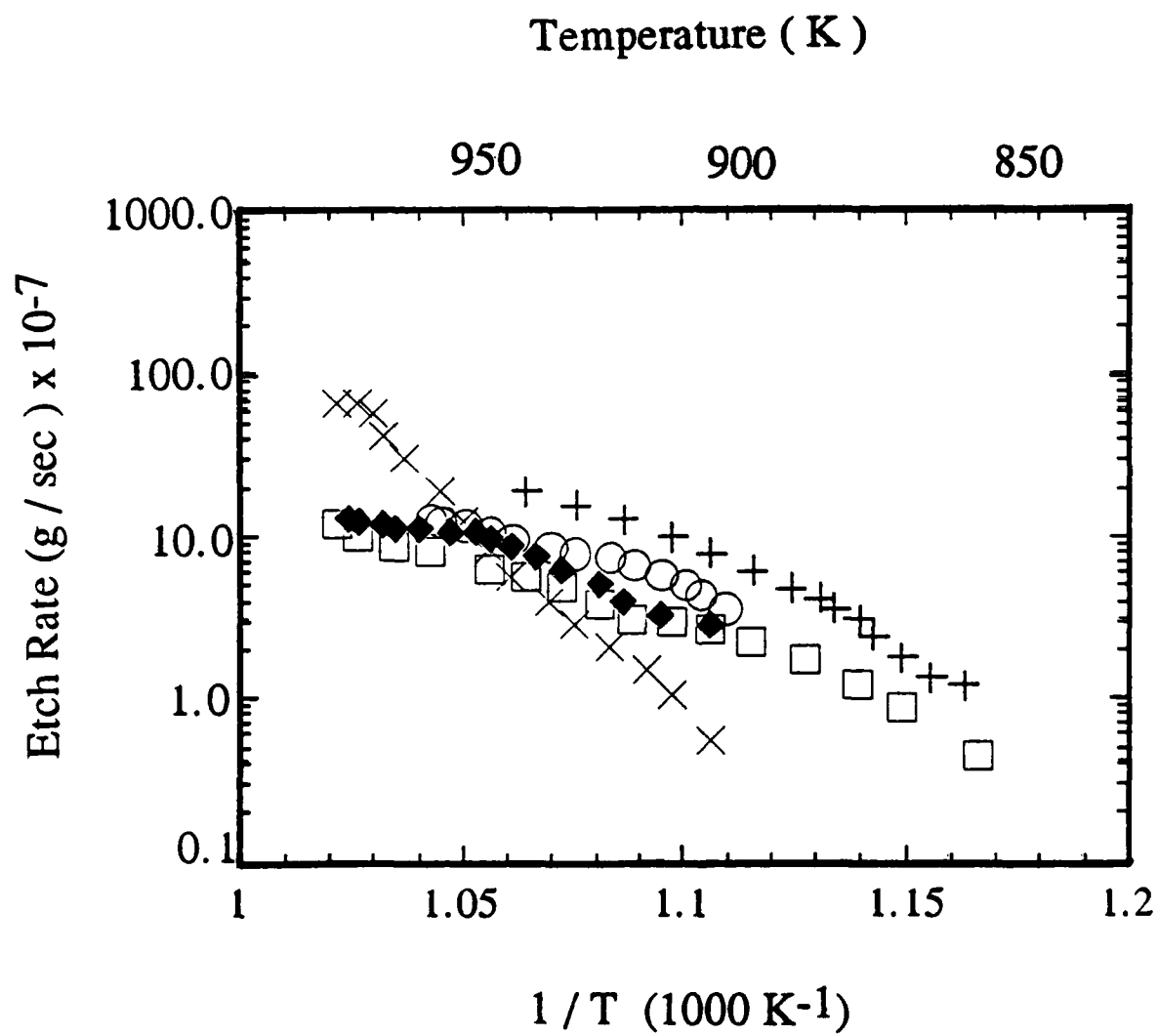
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