1 of 1

DIRECT MEASUREMENT OF THE REACTIVITY OF NH AND OH ON A SILICON NITRIDE SURFACE

R. J. Buss*, P. H⁺*, E. R. Fisher**, and William G. Breiland*

*Sandia National Laboratories, Albuquerque, New Mexico, 87185-0367

**Dept. of Chemistry, Colorado State University, Ft. Collins, CO 80523

ABSTRACT

In order to understand and successfully model the plasma processing used in device fabrication, it is important to determine the role played by plasma-generated radicals. We have used the IRIS technique (Imaging of Radicals Interacting with Surfaces) to obtain the reactivity of $\text{NH}(\text{X}^3\text{S}^-)$ and $\text{OH}(\text{X}^2\text{P})$ at a silicon nitride film surface while the film is exposed to a plasma-type environment. The reactivity of NH was found to be zero both during exposure of the surface to an NH_3 plasma and during active deposition of silicon nitride from a SiH_4/NH_3 plasma. No NH surface reaction was detectable for any rotational states of NH and over a surface temperature range of 300-700 K. OH radicals generated in an H_2O plasma were found to have a reactivity of 0.57 on a room temperature oxidized silicon nitride surface. The OH reactivity falls to zero as the temperature of the substrate is raised.

INTRODUCTION

The manufacturing processes used in the fabrication of microelectronic devices, such as chemical vapor deposition and plasma processing, often rely on very complex chemistries. With the continuing need to improve the performance of the processes, there is increased interest in understanding the chemistry so that accurate models can be developed. A detailed model of even a relatively simple plasma deposition such as a-Si:H from SiH_4 ¹ requires a great body of gas phase reactions, ion reactions, and gas-surface reactions. Chemists have developed a fairly good understanding of gas phase chemistry which allows the modeller to make reasonable guesses for reaction mechanisms and rates. In contrast, much less is known concerning the interaction of molecules at the surfaces of importance in microelectronics. The bulk of the knowledge about surface reactions concerns adsorption of stable molecules on metal surfaces. Of much greater concern to the plasma modeller is the reactivity of free radicals at insulator surfaces.

In 1989, we reported² results using a new experimental technique which allows direct measurement of the reactivity of radicals at a surface which is exposed to a plasma-like environment. IRIS (Imaging of Radicals Interacting with Surfaces) involves spatial imaging of laser-induced-fluorescence (LIF) from a plasma-generated molecular beam incident on a substrate in a high vacuum. During the experiment, the substrate is bombarded by the full range of plasma species, so it can be argued that the measured reactivity of a radical corresponds closely to radical behavior in the plasma itself.

The IRIS technique has been discussed in detail previously.²⁻⁵ Figure 1 shows the

MASTER

experimental configuration both as a planar view through the apparatus (upper) and as a 3-D view showing the spatial relationships of the components (lower). The method uses spatially resolved LIF to detect simultaneously molecules in a collimated, near-effusive molecular beam and molecules coming from a surface. The selectivity of the LIF is used to monitor one species in a molecular beam made from a rf plasma. Comparison of the LIF signals observed with the surface in and out of the path of the molecular beam yields the fraction of the incident molecules (of the species being detected) that react at the surface.

Figure 1. Two schematics of the IRIS experimental arrangement. Above is a top view of the apparatus. Below is a 3-D depiction of the spatial relationships of the components.

We report, here, measurements of the reactivity of $\text{NH}(\text{X}^3\text{S}^-)$ and $\text{OH}(\text{X}^2\text{P})$ at a silicon nitride film using IRIS. For the NH studies, either a pure ammonia or an NH_3/SiH_4 plasma is used as the NH source. In the OH reactivity studies, a pure water plasma acts as the OH source. The samples used for these experiments are 1 x 2 cm pieces of silicon with 158 Å

of thermally grown nitride. The substrate is placed parallel to the laser beam at a 43.3° angle relative to the molecular beam. For complete experimental details see ref 4 (NH) and ref 5 (OH).

RESULTS AND DISCUSSION

NH

The NH radical is completely unreactive at the silicon nitride surface under all experimental conditions. Under steady state bombardment of the substrate by the NH_3 plasma-beam, 100% of the NH flux to the surface is observed to rebound without reaction. The IRIS experiment yields the angular distribution of the desorbing radical. For all NH experiments, the desorbing NH has a cosine distribution, consistent with complete energy accommodation with the surface.

IRIS measurements at substrate temperatures ranging from 300-668K result in no increase in reactivity. The angular distribution of desorbing NH remains cosine over the entire temperature range. The LIF of NH is rotational state resolved and experiments with each of the $J=1,3$ and 5 states gave identical results (after correction for population changes resulting from thermal accommodation with the surface).

The pure ammonia plasma is neither an etching nor depositing process environment. There is continuous bombardment of the surface by ions and neutrals (eg. H, NH, NH_2 , and NH_3) and some transient initial chemistry transforms the surface termination to a steady-state condition. It is plausible that the surface is predominantly terminated by NH_x groups although unpaired electrons and physisorbed molecules are also expected. Although the chemistry of NH at surfaces is unknown, it is energetically possible for NH to insert into an NH bond ($\Delta H \sim -45$ kcal/mol) and very favorable to add to an unpaired electron (eg. $\text{NH} + \text{SiH}_3 \rightarrow \text{HNSiH}_3$, $\Delta H \sim -83$ kcal/mol). Other possible reaction paths include an NH molecule physisorbing and migrating to a reactive site or remaining adsorbed until a gas phase radical collides with it. We estimate, on the basis of the plasma pressure (30 mTorr) and the distance to the substrate (44 mm), that the collision frequency at a site on the surface is about 150/sec. Our observation that essentially all the incident NH desorbs without reaction shows that none of the suggested pathways have significant rates. When silane is added to the plasma and a film of $\text{a-SiN}_x\text{:H}$ is being deposited, the steady state surface coverage is expected to include SiH_x groups. Insertion of NH into an X_3SiH bond to give X_3SiNH_2 is energetically very favorable ($\Delta H \sim -110$ kcal/mol). Again we find that NH is unreactive with this surface, indicating that either the SiH_x groups are in very low steady-state concentrations or the insertion reaction has a very low cross section regardless of energetics. The insertion reaction for $\text{NH}(\text{X}^3\text{S}^\cdot)$ probably has a potential energy barrier because the electronic configuration is wrong.

OH

In contrast to the NH results, OH reacts to a significant extent on the room temperature substrate. The OH radicals present in the molecular beam generated from a pure H_2O plasma have a reactivity of 0.57 on the silicon nitride surface. The desorbing OH

(43% of the incident flux) has a cosine angular distribution suggesting complete thermal accommodation with the surface.

On heating the substrate, the reactivity decreases markedly such that by 475 K, essentially all of the OH desorbs unreacted. The reactivity remains zero at higher temperatures (to 723 K). The temperature dependence experiments are performed for each of six rotational states (0.5 to 5.5). The changes in intensity of scattered signal with rotational state agree well with a model of complete energy accommodation between adsorbed OH and the surface. That is, OH arrives at the surface with a rotational temperature characteristic of the plasma (340 K) and desorbs at the surface temperature.

The pure H₂O plasma, similar to the NH₃ case, neither etches nor deposits a film on the silicon nitride. Auger and XPS measurements of the silicon nitride after exposure to the plasma indicate that the surface has been converted to the more thermodynamically stable oxide⁶. The surface reactions between silicon oxide and water have been the subject of many studies⁷. It is generally believed that, in vacuum at room temperature, a silica surface exposed to water is predominantly terminated by silanol groups. During continuous exposure of the sample to the plasma the surface is apparently converted to an oxide, and, at steady state, the surface presumably has a high surface coverage of silanol groups.

A simple model to explain the temperature dependence of the reactivity of OH is a competition between the desorption of physisorbed OH and its loss through reaction on the substrate⁵. The most probable reaction is the abstraction of hydrogen from a silanol group to give water. The silanol group is later regenerated by reaction with other plasma species (eg. H atoms). The net effect of this model is a temperature-dependent consumption of OH by reaction at the surface, but no net deposition or etching. At room temperature, the adsorbed OH remains on the surface long enough for 57% to find silanol groups and react, whereas, at high temperatures, the residence time becomes shorter and desorption predominates.

In conclusion, we have found that NH is completely unreactive at a silicon nitride surface exposed to NH₃ and SiH₄/NH₃ plasmas. The reactivity of OH on a surface exposed to a water plasma is high, but the reaction does not involve deposition or etching. It is clear that more work is needed to develop general principles governing the reaction of radicals at surfaces.

ACKNOWLEDGMENTS

This work was performed at Sandia National Laboratories and was supported by the U.S. Department of Energy under contract No. DE-AC04-94AL85000, partially from the Office of Basic Energy Sciences, and partially from the Office of Defense Programs through a Technology Transfer Initiative joint program with Texas Instruments. We also thank Pamela Ward for her technical assistance.

REFERENCES

- (1) Kushner, M. J. *J. Appl. Phys.* **1988**, *63*, 2532.
- (2) Ho, P.; Breiland, W. G.; Buss, R. J. *J. Chem. Phys.* **1989**, *91*, 2627.

- (3) Buss, R. J.; Ho, P.; Weber, M. E. *Plasma Chem. Plasma Process.* **1993**, *13*, 61.
- (4) Fisher, E. R.; Ho, P.; Breiland, W. G.; Buss, R. J. *J. Phys. Chem.* **1992**, *96*, 9855.
- (5) Fisher, E. R.; Ho, P.; Breiland, W. G.; Buss, R. J. *J. Phys. Chem.* **1993**, *97*, 10287.
- (6) Rochow, E. G. *Chemistry of the Silicones*; John Wiley and Sons: London, 1951.
- (7) Iler, R. K. *The Chemistry of Silica*; John Wiley and Sons: New York, 1979.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DATE

FILMED

3 / 8 / 94

END