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## Etching of Al and Cu Solids by SiCl<sub>4</sub> Molecules

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The classical trajectory method, previously applied to the reactions of polyatomic molecules with fcc structured metal solids[S. C. Park, C. H. Cho, and C. H. Rhee, *Bull. Kor. Chem. Soc.*, **11**, 1(1990)]<sup>1</sup> is extended to the collision energy dependence of the reaction of the Al solid by SiCl<sub>4</sub> molecules. We have calculated etching yields, degrees of anisotropy, kinetic energy distributions, and angular distributions for the reactions of the Al solid and compared with those for the reactions of the Cu solid. Over the range of collision energies we considered, the reactions of the Al solid show higher etching yield and better anisotropy than the reactions of the Cu solid. Details of reaction mechanisms and the relevance of these calculations for the dry etching of CuAl alloy are discussed.

### Introduction

The study of plasma assisted chemical reactions on metal and semiconductor solids has received extensive attention in recent years.<sup>1-10</sup> The main reason for this is that reactive sputter etching is a widely used process in the micro-fabrication of VLSI (very-large-scale-integrated circuits) and ULSI (ultra-large-scale-integrated circuits). As the dimensions of the VLSI and ULSI chips are reduced, and the number of components per chip increased, the degree of control over the manufacturing processes must necessarily be improved.<sup>11-14</sup> This may only be achieved by a detailed understanding of the mechanisms involved in each of the many steps, such as ion implantation, diffusion, oxidation, film deposition, lithography, etching, etc. required to make VLSI and ULSI chips. This micro-world, the potential of which can hardly be fully appreciated even today, has a direct appeal to all those of scientific inclination. However, the role of chemistry in the creation of this world becomes clear only on closer examination of the manufacturing processes. Chemistry plays a key role not only in the understanding of fundamental reactions for the processes, but also in the mass production of semiconductors containing integrated components.

Plasma reactions on metal solids are an important class of reactions in the industrial manufacture of VLSI chips.<sup>11-14</sup> Extensive theoretical and experimental studies of plasma reactions on copper solid have been reported<sup>15-24</sup> and have proposed detailed sputtering mechanisms.<sup>23,24</sup> Key reactions on metal etching in the complementary metaloxide semiconductor (CMOS) micro-fabrication are the reactions of Cu, Al and Cu-Al alloys with polyatomic gas plasmas such as SiCl<sub>4</sub>, CCl<sub>4</sub>, BCl<sub>3</sub> and mixtures of these gases with Cl<sub>2</sub>.<sup>12,25</sup> One of the most difficult problems in CMOS micro-fabrica-

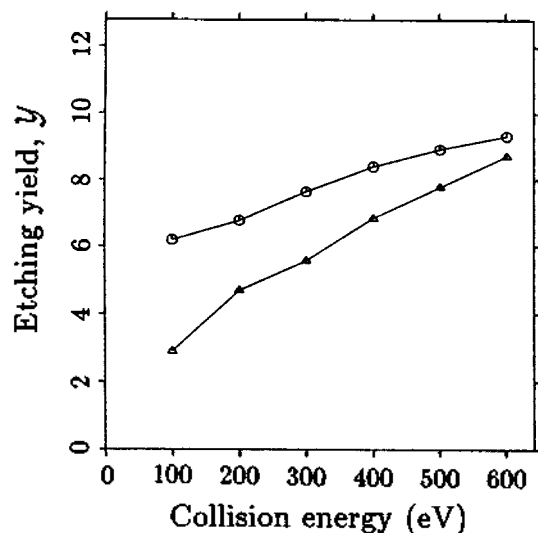
tion is the etch of Cu and Al solids which is essential in the CMOS fabrications. Although extensive research and development have been pursued for the reactions in manufacturing point of view, one has not yet found efficient and proper ways of the etching of Cu and Al solids and Al-Cu alloy. It does require the fundamental understanding for the reactions. In spite of the importance for these reactions, not only in industrial interests but also in the fundamental interest of basic science, very little detailed experimental investigation of the reaction on Al solids and Cu-Al alloys has been done, and the mechanisms involved are unknown. Hence there is a need for theoretical investigation of these systems.

This is the second paper in the series of a classical trajectory study of etch reactions on metal surfaces. In the first paper<sup>1</sup>, the classical trajectory method for an application to reactions of polyatomic molecule with a fcc metal solid has been employed and has tested to a model Al+SiCl<sub>4</sub> reaction at collision energy 600 eV. In this paper, we present the collision energy dependence of the etch reactions of the aluminum solid by SiCl<sub>4</sub> molecules and compare with the reactions of the copper solid by SiCl<sub>4</sub> molecules previously reported by Park *et al.*<sup>3</sup> A model SiCl<sub>4</sub>+Al(001) system is employed to calculate etching yields, the nature of products of the reactions, and the energy and angular distributions of the products.

A brief review of the theory, and a discussion of the interaction potential and calculation details are given in the next section. The results and discussion are presented in Sec. III. Conclusion and remarks are contained in Sec. IV.

### Theory and Calculations

The approach used here to treat the reactions of the Al



**Figure 1.** Collision energy dependence of etching yields for the Al(O) and the Cu(Δ)<sup>3</sup> solids.

**Table 1.** Calculated Etching Yields, Mean Kinetic Energy and Degree of Anisotropy

Initial kinetic Energy/eV	SiCl <sub>4</sub> +Al(001)			SiCl <sub>4</sub> +Cu(001)*		
	y	<K.E.)/eV	A <sub>r</sub>	y	<K.E.)/eV	A <sub>r</sub>
100	6.19	2.58	-0.125	2.89	2.33	-0.33
200	6.77	2.82	-0.150	4.70	3.22	-0.30
300	7.64	3.43	-0.165	5.58	4.27	-0.33
400	8.40	3.78	-0.005	6.84	4.70	-0.21
500	8.92	4.74	-0.045	7.79	5.52	-0.24
600	9.32	5.13	-0.044	8.72	6.05	-0.23

\*From reference 3.

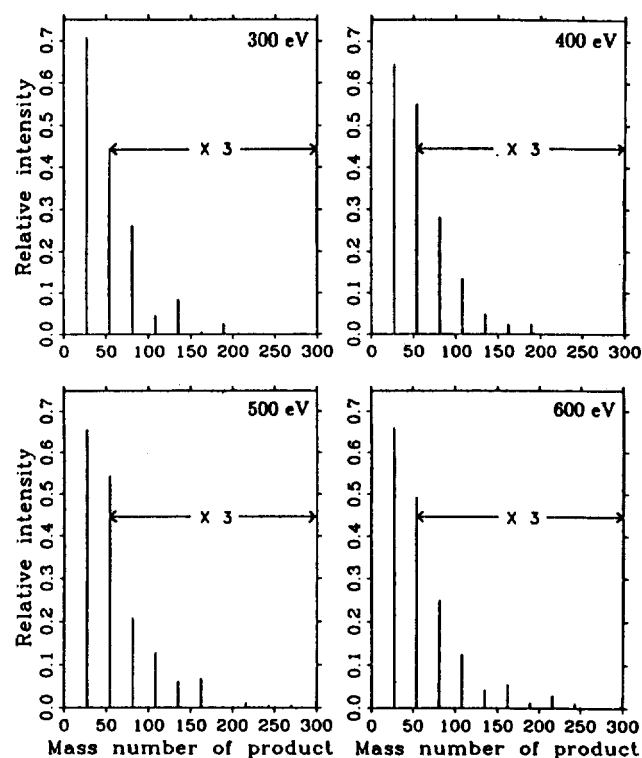
solid by SiCl<sub>4</sub> molecules is based on the classical trajectory method which has been discussed elsewhere.<sup>26-28</sup> Extensive derivations for the equations of motions and the formation of products and its application to fcc solids with polyatomic reactions have been described in the previous work<sup>1</sup>, so we do not present the details here.

The interaction potentials we have used in the calculations are pairwise sum of Born Mayer-Spline-Morse functions for the solid atoms. The interactions between incident SiCl<sub>4</sub> molecules and Al solid atoms, and Si-Cl and Cl-Cl interactions in SiCl<sub>4</sub> molecules are described by pairwise sum of Morse potentials. We have considered only two body terms and do not take into three body interaction terms. Details of the functional form of the potentials and their parameters have been presented in the previous work.<sup>1</sup>

At a given initial collision energy, we set up the initial conditions which are the initial positions and momenta for all atoms in whole collision system. Details of coordinate system and its initial conditions have also been described previously. 400 trajectories are propagated for a given collision energy to make ensemble average of the final results.

## Results and Discussion

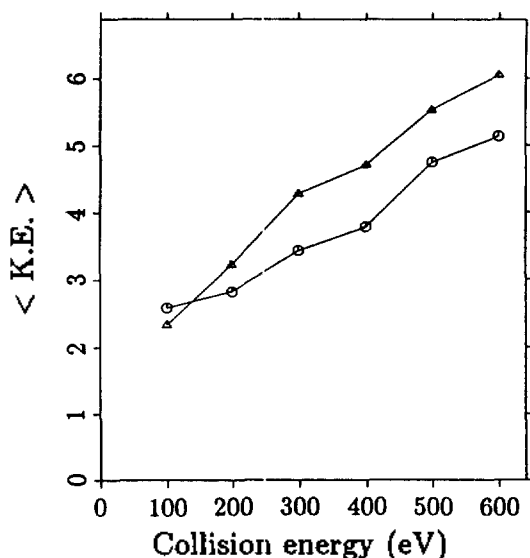
First, we have calculated the etching yields of the aluminum solid by SiCl<sub>4</sub> molecules and compared with the reaction of the copper solid with SiCl<sub>4</sub> by Park *et al.*<sup>3</sup> The etching yields for these two reactions are given in the Figure 1 and Table 1. Figure 1 shows the initial beam kinetic energy dependence of etching yield of the aluminum solid by SiCl<sub>4</sub> molecules together with the copper solid previously by Park *et al.*<sup>3</sup> The etching yields of the both solids increase with increasing beam kinetic energies. This is a quite general phenomena in a sputter etching experiment.<sup>23,24,29,30</sup> The calculated etching yields of the Al solid are greater than those of the Cu solid over the range of the beam kinetic energies we considered as we expected. However, the increasing rate, with respect to initial beam kinetic energy, of etching yields for the Al solid is lower than that of the Cu solid. At the



**Figure 2.** Product distributions of the reaction of Al(001)+SiCl<sub>4</sub> for the initial beam kinetic energy, 300-600 eV. Relatively intensity vs. mass numbers of products(amu) are plotted.

beam kinetic energy 100 eV, the etching yield of the Al solid and the Cu solid is 6.19 and 2.89 respectively, whilst the etching yield of these two solids is 9.32 and 8.72 respectively at 600 eV.

To understand the difference of the etching yields and more details of reaction mechanisms, we have calculated the product distributions for the etching of the aluminum solid by SiCl<sub>4</sub> molecules, which are shown in the Figure 2 for four different initial beam kinetic energies. The major products for the reaction of the Al solid are aluminum monomers and dimers together with considerable amounts of multimers as shown in the Figure 2. The initial beam kinetic energy dependence of the product distributions does not change quite much, but the products of multimers vary significantly with initial beam kinetic energies. No chlorine compounds



**Figure 3.** Collision energy dependence of the average kinetic energies of the ejected atoms for the reaction systems of the Al(O) and the Cu( $\Delta$ )<sup>3</sup> solids.

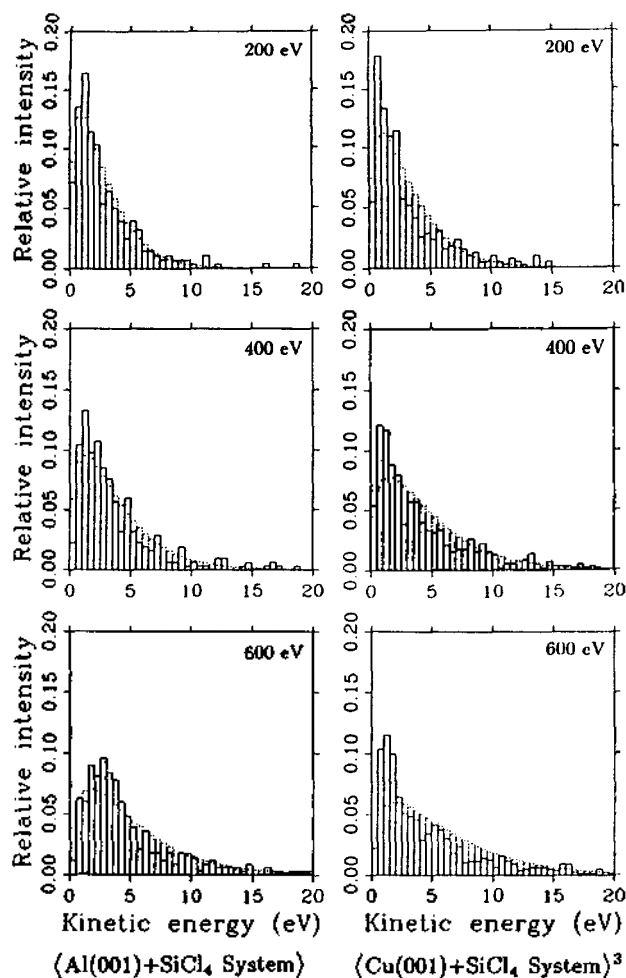
are ejected in the calculations. These results are quite different from those of the reaction of the copper solid by SiCl<sub>4</sub> molecules by Park *et al.*<sup>3</sup> In the reaction of the copper solid, the major products are atomic Cu together with trace quantities of copper multimers. Although they did not detect chlorine compounds in the reactions, the CuCl and CuCl<sub>2</sub> molecules were detected to be intact on the surface. However the AlCl, AlCl<sub>2</sub> and AlCl<sub>3</sub> are not detected even on the surface of the Al solid in the reactions. We have found that all the chlorine atoms penetrate a few layers of the Al solid. This means that the reaction mechanisms of the Cu and the Al solids with SiCl<sub>4</sub> molecules are quite different. In the reaction of the Cu solid, the chlorine atoms are dissociated from the SiCl<sub>4</sub> molecules and react with Cu atoms to remain intact on the Cu solid. In the reaction of the Al solid, on the other hand, the chlorine atoms are dissociated and penetrate into the Al layers. This can be easily understood with the structures and the interaction potentials of the Cu and the Al solid. The nearest neighbor distance of the Cu and the Al solids is 2.556Å and 2.850Å respectively, and the interaction between Cu-Cu atoms in the Cu solid is stronger than that between Al-Al atoms in the Al solid. The binding energy of the Cu-Cl bond and the Al-Cl bond is 3.93 eV and 5.12 eV respectively. Therefore, the chlorine atoms can easily penetrate to the Al solid layers due to the less tighter interaction of the Al-Al and the more bulky structure of the Al-Al distance than that of the Cu solid. Furthermore the binding energy of the Al-Cl bond is greater than that of the Cu-Cl, which does allow the Cl atoms to stay inside the Al solid layers more than in the Cu system. This is consistent with the fact that the average kinetic energies of the ejected Al atoms shown in the Figure 3 are less than those of the Cu atoms over the range of initial kinetic energies we considered. Owing to the greater binding energy of the Al-Cl bond than that of the Cu-Cl, large amount of the initial beam kinetic energies are partitioned to Al-Cl interaction when the Cl atoms exist in the layers of the Al

solid. This gives less kinetic energy to the ejected Al atoms than to the ejected Cu atoms.

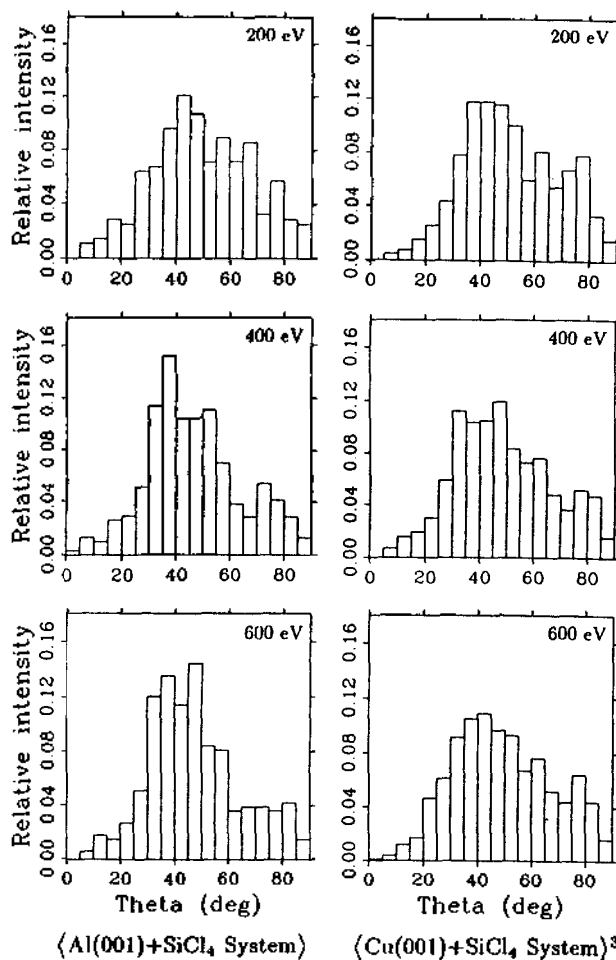
The lower values of the Cu etching yields shown in the Figure 1 are due to the residues of the CuCl and CuCl<sub>2</sub> which reflect the ejecting Cu atoms from the inner layer by indirect collision back to the inner layer direction. On the other hand, Al atoms can be ejected without reflection of residue due to non-existence of residues in the Al system. This is quite consistent with the problem<sup>12,25</sup> in VLSI micro-fabrication where the sputter etching of CuAl and CuAlSi alloys gives rise to involatile copper chloride residues forming on the surface when the copper concentration is high (*e.g.* >4%).

We also have calculated the degree of anisotropy, *A*, for the reaction of the Al solid by SiCl<sub>4</sub> molecules and have compared with that of the Cu solid, which are shown in the Table 1. The collision energy dependence of the degree of anisotropy does vary with collision energy, but we cannot find out real significance. Neither of these systems give good anisotropic sputter etching according to the definition of Mogab.<sup>12</sup> However, the reactions of Al solid give relatively better anisotropy than the reactions of Cu solid over the range of collision energies we considered. This is also consistent with the problem<sup>12,25</sup> in the CMOS micro-fabrication of the CuAl and the CuAlSi alloys where the degrees of anisotropy are getting worse with increasing concentration of the copper atoms. This may be due to the fact that the residues of the CuCl and CuCl<sub>2</sub> scatter the ejected Cu atoms to parallel direction in the reactions of the Cu solid. However, the Al atoms can be ejected more freely to the perpendicular direction than the Cu atoms, since there are no residues in the reactions of the Al solid. Although the expression of the degree of anisotropy defined by Mogab<sup>12</sup> can describe anisotropy of experimental results and we can also calculate the degree of anisotropy in theoretical reaction dynamics, *e.g.* classical trajectory calculations, it is very difficult to explain actual anisotropy of the reaction systems in theoretical dynamics calculations. One of the possible reasons is that the expression of the anisotropy in experimental results can represent the position space of the reacted solid, while the dynamics calculation of the degree of anisotropy is based on the momentum space in the reaction system. We have thought that one can/should develop a proper mathematical transformation of the momentum representation to the space representation of the degree of anisotropy for the reaction system. It is a new challenge in theoretical work in this field of research.

The kinetic energy distributions of ejected Al atoms are shown in the Figure 4 for three different initial beam kinetic energies, 200 eV, 400 eV, and 600 eV together with those for the reactions of the Cu solid. The solid histograms represent the results of kinetic energies of ejected Al atoms by binning, and the dashed ones are for the Maxwell-Boltzmann distributions obtained at the temperatures which have been calculated from data of the average kinetic energies of ejected atoms shown in the Figure 3. Several features of the kinetic energy distributions are apparent. The peaks of the kinetic energy distributions of ejected atoms are 1.5-3.0 eV and 0.5-1.5 eV with increasing beam kinetic energies for the Al solid and the Cu solid respectively. A simple classical theory of energy distribution,<sup>31,32</sup> which is independent of



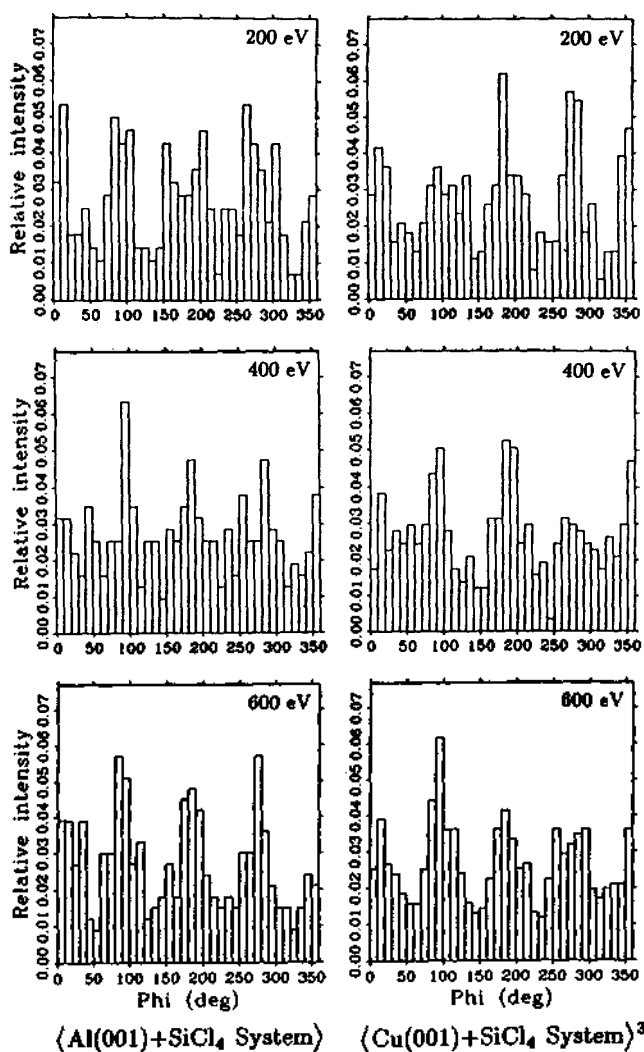
**Figure 4.** Histograms of the kinetic energy distributions of ejected atoms for the initial beam kinetic energies, 200, 400, and 600 eV for the reactions of the Al and the Cu solids. The solid histograms represent the results by binning, and the dashed ones are for the Maxwell-Boltzmann distributions. Bin size is 0.5 eV.



**Figure 5.** Histograms of the polar angle distributions of ejected atoms for initial beam kinetic energies, 200, 400, and 600 eV for the reactions of the Al and the Cu solids. Bin size is 5°.

the incident ions and molecules and does not take into account, predicts a maximum at  $E_b/2$ , where  $E_b$  is the binding energy of an atom to the solid surface. This gives predicted peaks at about 2.6 eV and 1.8 eV for the Al solid and the Cu solid respectively, in reasonable agreement with both systems considering the approximation made in the theory. The shapes of the energy distributions of the ejected atoms resemble the Maxwell-Boltzmann distribution curves as were the cases of the other systems both in experiment<sup>29,30</sup> and theoretical calculations.<sup>3,4,15,16</sup> Over the range of beam kinetic energies we considered, the energy distributions of the ejected Al atoms are relatively fitted better than those of the Cu system, to the Maxwell-Boltzmann distribution. For the reaction of the Al solid, they are fitted better in higher collision energies. It is difficult to define surface temperatures accurately for these cases. However, the peaks of energy distributions for the Al system are broad and are located at the higher values (1.5-3.0 eV) than those for the Cu system (0.5-1.5 eV) in the range of initial beam kinetic energies 100 eV to 600 eV. These indicate that the temperatures of the Al solids are significantly higher than those of the Cu

solids. These hotter surfaces of the Al reactions may be due to the fact that the excitation is easier for the weaker and longer Al-Al bond, which in turn could produce the more violently moving free Al atoms in the solids than in the case for the tighter and shorter Cu-Cu bond. The reason for the better fit of the energy distributions of the ejected Al atoms into the Maxwell-Boltzmann distribution curves is that the tendency for the Al solid to reach the thermal equilibrium during the reactions is increased because of the existence of penetrated chlorine atoms in inner layers of the Al solids. When the dissociated chlorine atoms penetrate into inner layers of the Al solids, those chlorine atoms cause the radiation damage in the layer, and then the resulting ejection of atoms could take place. However, in the case of the Cu solid, the possibility of this radiation damage is relatively lower than in the Al solid because of lower penetration of chlorine atoms. The majority of the ejected Cu atoms come from the direct collision process. Since the direct collision produces the more energetic free atoms than the indirect process (the radiation damage), the average kinetic energies of the Cu system should have higher values than those of the Al system. This is quite consistent with the Figure 3 where the average kinetic energies of the ejected Cu atoms have higher values than those of the Al atoms over the range



**Figure 6.** Histograms of the azimuthal angle distributions of ejected atoms for initial beam kinetic energies, 200, 400, and 600 eV for the reactions of the Al and the Cu solids. Bin size is  $10^\circ$ .

of initial beam kinetic energies. It could be explained as follows. The sudden, non-adiabatic ejection of the Cu atoms with little or no coupling to the rest of the solid might have caused the steeper rise and faster decay in the energy distribution curves for the Cu system and the resulting deviation from the Maxwell-Boltzmann distribution curves shown in the Figure 4.

Figure 5 shows the polar angular distributions of the ejected Al atoms by  $\text{SiCl}_4$  molecules for the initial beam kinetic energies, 200 eV, 400 eV, and 600 eV together with those of the Cu solids. The polar angular distributions of the Al solids and the Cu solids do not vary quite much with increasing initial beam kinetic energies. It is difficult to find out real significance for the dependence of initial beam kinetic energies in the polar angular distributions. This is similar to the degree of anisotropy as explained already. The polar angular distributions indicate that large amounts of parallel momentum are transferred to the ejected atoms during the collision processes. In the distributions of the Al solid, the number of the ejected Al atoms at angles less than  $45^\circ$  is

more than that of atoms with angles greater than  $45^\circ$  over the range of initial beam kinetic energies we considered. However, the distributions of the Cu solid are opposite as shown in the Figure 5. This is consistent with the fact that the anisotropy of the reactions of the Al solid is better than that of the reactions of the Cu solid shown in the Table 1.

The azimuthal angular distributions for the reactions of the Al solid are shown in the Figure 6 together with those of the Cu system. Over the range of initial collision energies we considered, the shapes of the distributions do not change significantly with initial beam kinetic energies. The distributions of the azimuthal angles are quite structured with sharp maxima and minima. The locations of the maxima and minima on the azimuthal angular distributions are related to the symmetry directions of the Al and the Cu solids. Overall shapes of the distributions for the two solids are quite similar. Those are due to same symmetry properties of both solids in the fcc structure. The four maxima at  $90^\circ$ ,  $180^\circ$ ,  $270^\circ$  and  $360^\circ$  arise from the ejected atoms preferentially ejecting in the direction of the fourfold holes surrounding them<sup>24</sup>. Similarly, the minima at  $45^\circ$ ,  $135^\circ$ ,  $225^\circ$  and  $315^\circ$  arise correspond to the four nearest neighbors in the first layer. Similar symmetry-related angular distributions have been reported in calculations by Garrison and coworkers<sup>15,19,21</sup> and have been observed experimentally by various groups<sup>7,29</sup>. Comparing with the Al and the Cu systems, the distributions of the reaction of the Al solid are relatively less distinctive structure than those of the reaction of Cu system. Especially, collision energies at 200 eV and 400 eV, the Cu solids give more distinctive structures to the symmetry directions. These are due to the fact that the Al solids have more experience in radiation damage than the Cu solids, while the reactions of the Cu solids have more direct process.

## Summary

The classical trajectory method has been extended to perform computer simulation on the sputter etching of an Al solid at the range of collision energies 100 eV to 600. Etching yields, degrees of anisotropy, kinetic energy distributions and angular distributions have been calculated. The calculated results are compared to those of the Cu system.<sup>3</sup> The etching yields of the reactions of both solids increase with increasing collision energy. The reactions of the Al solid give higher etching yields and better anisotropy than the reactions of the Cu solid. The major products of the reaction of the Al solid are aluminum monomers, dimers and considerable amounts of multimers, which are quite different from those of the Cu solid. These indicate that the reaction mechanisms of those systems are quite different.

The following are major differences in reaction mechanisms in both systems. In the Al system, the dissociated chlorine atoms penetrate into the inner layers which cause radiation damage to the Al solid, while in the Cu system the dissociated chlorine atoms react with Cu atoms and form involatile residues,  $\text{CuCl}$  and  $\text{CuCl}_2$  which remain intact on the surface. These residues cause the lower etching yield and higher anisotropy in the case of the Cu solid. These are consistent with the problem<sup>2,12</sup> in the CMOS micro-fabrication of the CuAl and CuAlSi alloys. Effects of amorphous

structures on the reactions of both solids have been suggested by an experimentalist<sup>35</sup>. These are currently under progress in our group and will be reported elsewhere soon.

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## A Shapiro Reaction with N,N-Diethylaminosulfonylhydrazones

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A modified Shapiro reaction was developed using N,N-diethylaminosulfonylhydrazones.

### Introduction

The formation of alkenes from the reaction of arylsulfonylhydrazones with strong bases such as alkylolithiums (Shapiro reaction), has proved to be a useful reaction and has been subject of numerous studies<sup>1,2</sup>. Following the initial depro-

tonation at the amide nitrogen of arylsulfonylhydrazones, the second proton abstraction occurs at the  $\alpha$ -carbon *syn* to the sulfonylamide group<sup>3,4</sup>, which has been attributed to the chelation effect<sup>5,6</sup> and a  $6\pi$ -electron non-bonded through-space interaction<sup>7</sup>. Since a strong steric bias exists in the stereochemistry of tosylhydrazones prepared from unsymmetrical