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Publication Date

1990-08-01

Center for Advanced Materials

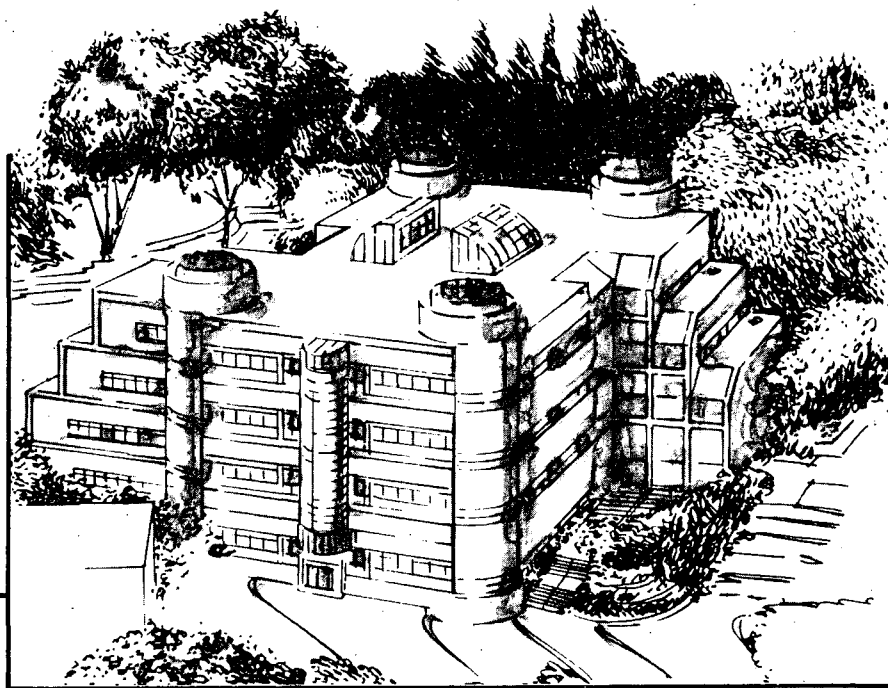
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Presented at the American Society of Metals International's
3rd Electronic Materials & Processing Congress,
San Francisco, CA, August 20-24, 1990,
and to be published in the Proceedings

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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Study of Copper Diffusion into Polyimides
by Optical Second Harmonic Generation

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Abstract

Formation of Cu clusters deposited on polyimide and their diffusion into polyimide have been studied in-situ by the surface-sensitive second harmonic generation (SHG) technique. The diffusion coefficients of Cu clusters were measured and compared with those for atomic Cu. The effectiveness of a titanium (Ti) intermediate layer in preventing Cu diffusion into PI was also investigated. It was found that an atomic layer of Ti was already sufficient for arresting the diffusion process.

1. Introduction

In recent years, polyimides have emerged as a strong contender for use as an interlayer dielectric material in the VLSI packaging technology. The metal/polyimide structure-property relation of metal bonding to polyimide, therefore, has become an important area of research. Most studies to date have concentrated on the interfacial chemical reactions¹⁻⁶, and mechanical and adhesive properties.⁷⁻⁹ As a general rule, interdiffusion of species at the metal/polyimide interface plays an important role in controlling the properties of the interface. Several advanced techniques have been used for these diffusion studies, such as Rutherford backward scattering (RBS)¹⁰⁻¹¹, transmission electron microscopy (TEM)¹²⁻¹³, and radiotracer (RT) technique in combination with low energy ion sputtering¹⁴. The accuracy of these measurements is often limited by either the depth resolution (in RBS)¹⁰⁻¹¹, or possible errors introduced by the surface roughness of the processed polyimide samples which measured to be 300 Å (in RT)¹⁴. Therefore, the measured diffusion coefficients appeared to vary from technique to technique. Furthermore, metal clusters could be formed at the interface. They

can affect the diffusion, but they are difficult to detect by techniques such as RBS and RT.

Optical second harmonic generation (SHG)¹⁵ has recently been demonstrated to be a very sensitive surface and interface specific diagnostic tool. It can be used to study metal cluster formation and diffusion into polyimide (PI) by monitoring the signal in-situ and as a function of time. The technique possesses a number of relevant advantages: the experimental arrangement is simple; the output can be easily discriminated by spectral and spatial filtering against background luminescence and elastic scattering; it is sensitive to submonolayers of atoms or molecules adsorbed at a surface or interface; it has inherently high spatial, temporal and spectral resolution; it is capable of nondestructive and remote sensing of surfaces and interfaces; and the technique can be used to study buried interfaces accessible by light.

For the problem addressed here, the highly sensitive SHG and its ability to perform *in-situ* measurements allow a mechanistic study of diffusion and formation of metal clusters at polyimide surfaces. It is known that SHG can be enhanced by surface roughness and is sensitive to the size of metal grains at the surface¹⁶⁻¹⁷. On the other hand, SHG will eventually decrease as the metal deposition on the surface disappears into the polyimide bulk by diffusion. In this paper, we report our recent diffusion measurements of Cu into a fully cured polyimide at different temperatures using SHG. The formation of Cu clusters on the surface obviously impedes the diffusion of Cu, into polyimide. We also observe the effect of an intermediate titanium (Ti) layer as a diffusion barrier at a Cu/PI interface. A monolayer of Ti appears to be already sufficient to restrict Cu diffusion into PI.

2. Theoretical

Second-order nonlinear optical effects, such as second harmonic generation (SHG), are forbidden (under the electric-dipole approximation) in a medium with inversion symmetry. Since the inversion symmetry is necessarily broken at a surface, such nonlinear effects appear to be highly surface-specific for interfaces between two centrosymmetric media¹⁸. The metal/polyimide interface is an example. The SH intensity from a surface in the reflected direction can be expressed as¹⁹

$$S(2\omega) = \frac{32\pi^3\omega \sec^2\theta}{hc\epsilon} \left| \vec{e}^-(2\omega) \cdot \vec{\chi}_{s,eff}^{(2)} \cdot \vec{e}^-(\omega) \vec{e}^-(\omega) \right|^2 I^2(\omega) A T \quad (1)$$

where $I(\omega)$ is the pumping laser intensity, A is the beam cross-section, T is the laser pulse width, θ is SHG reflection angle, ϵ is the dielectric constant of the medium, $\vec{\chi}_{s,eff}^{(2)}$ is the effective surface nonlinear susceptibility, which is proportional to the surface number density of the nonlinear medium. The vectors $\vec{e}^-(\omega)$ are related to the unit polarization vectors $\hat{e}$ in the medium by the Fresnel coefficients

$$\vec{e}^-(\omega) = \vec{L} \cdot \vec{e}(\omega) \quad (2)$$

More generally, $\vec{L}$ acts as a local-field correction factor. On a rough metal surface with structure of the order of a wavelength, $\vec{L}$ can be strongly enhanced through the plasma resonance, leading to a surface enhancement of SHG by several orders of magnitude stronger than that from a smooth surface.²⁰

On the theory of diffusion, we can treat the diffusion of Cu into a polyimide as one-dimensional. The equation for diffusion with a constant diffusion coefficient D is²¹

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} \quad (3)$$

where $C(x, t)$ is the concentration of diffusing particles at position x and time t . We assume $C=C_0$ at $t=0$ for $0 < x < h$. The solution of the equation takes the form

$$C(x, t) = \frac{1}{2} C_0 \left[\operatorname{erf} \left(\frac{x-h}{\sqrt{4Dt}} \right) + \operatorname{erf} \left(\frac{x}{\sqrt{4Dt}} \right) \right] \quad (4)$$

We are interested in finding $\int_0^h \vec{C}(x, t) dx$ so that the diffusion coefficient D of the particle can be deduced. This can be achieved by SHG measurements. Since SHG is surface specific and the contribution from the polyimide substrate is negligible compared with that from Cu particles on the substrate, we, therefore, have the SHG signal given

$$S(2\omega, t) \propto \left| \int_0^h C(x, t) dx \right|^2 \approx \left| C\left(\frac{h}{2}, t\right) h \right|^2 \quad (5)$$

assuming that the variation of $C(x, t)$ in the region $0 < x < h$ is not very significant. By measuring $S(2\omega, t)$ and fitting data with Eqs. (4) and (5), we can then obtain the diffusion coefficient D .

As mentioned earlier, on a surface consisting of metal clusters, SHG can be significantly enhanced due to the macroscopic local-field enhancement¹⁶. The enhancement increases with the size of clusters and is around the maximum when the size is on the order of the laser wavelength in the metal. An enhancement of 10^3 - 10^4 by Ag clusters on substrates relative to a smooth Ag surface has been observed¹⁶. A similar effect, though not as large, is expected for Cu. With either a high evaporation rate of Cu on polyimide, or by heating up a Cu-covered polyimide substrate, it is known that Cu clusters (or islands) can be formed. The appearance of these clusters on polyimide and their possible diffusion into polyimide at temperature higher than the glass transition temperature (T_g) of the polyimide can be monitored by SHG.

3. Experimental arrangement

The samples were prepared by spin-coating polyimide material [DuPont 2566 or material provided by Digital Equipment Corporation (DEC)] into a thin layer form (between 1 and 10 μ) on a glass plate. The samples were then annealed at 360°C (or 390°C for DEC samples) in an inert gas to complete the imidization process. For the SHG measurement a sample was mounted into an ultra-high vacuum (UHV) chamber with a base pressure of 1×10^{-9} torr. It was heated to 300-360°C for several hours to desorb water from the polyimide before depositing metal on polyimide sample. Metal could be deposited by evaporation on the cleaned polyimide at either the room temperature or some selected temperatures.

The SHG experiment was carried out by a commercial Q-switched and mode-locked YAG laser system (Quantronix 416) with output at 1.06 μm . The laser beam was split into two. The beams were slightly focused and then directed onto the two surfaces of the sample with a fluence less than $1\text{mJ}/\text{cm}^2$. The incident angle was 75° from the metal side and 50° from the PI side. This arrangement allowed us to investigate simultaneously both the metal/PI interface and the metal/vacuum interface during or after the metal deposition. The SH beams in the reflection directions were detected separately by two photo-detection systems. We used a photo-counting technique in our detection because of the relatively low SH signals.

4. Results and Discussion

By either depositing Cu on a polyimide sample at an elevated temperature or by depositing at room temperature and then ramping the temperature up, one expects to have diffusion of Cu into polyimide and formation of Cu clusters (or islands) on the polyimide surface. Both processes could be simultaneously present, but one of them may become dominant under certain conditions. It has been reported that the diffusion coefficient of Cu atoms into polyimide is around 1×10^{-15} to $1 \times 10^{-14} \text{ cm}^2/\text{s}$ at $T=500$ to 600°K ¹⁴. This means that it takes only a few minutes for one monolayer of atomic Cu to diffuse into the bulk at 500°K . We can use SHG to monitor in-situ such an atomic diffusion. With approximately a monolayer of Cu deposited on a polyimide at 475°K (or deposited at room temperature and then heated to 475°K in two minutes), we observed first a rapid drop in SHG intensity in 2 minutes then a much slower decay, and finally a constant signal level. The initial drop is due to atomic diffusion into polyimide. The subsequent slower decay can be attributed to diffusion of small clusters into polyimide, and the constant signal level to large Cu clusters remaining on the surface. These clusters could be formed during evaporation and/or via Cu diffusion on the surface.

When Cu was deposited on polyimide at 675°K ($>T_g \approx 595^\circ\text{K}$), only a slow decay of SHG due to the diffusion of Cu clusters into polyimide was observed with our time resolution. Figure 1 is an example. A diffusion coefficient $D(T)$ of about $1 \times 10^{-16} \text{ cm}^2/\text{s}$ is inferred by the data using Eq. (5). It is about one or two orders of magnitude lower than that for the atomic diffusion¹⁴ but is close to that measured by RBS with Cu implanted in

polyimide by ion sputtering.¹⁰ In the latter process, it is known that Cu clusters were formed in the implantation process.

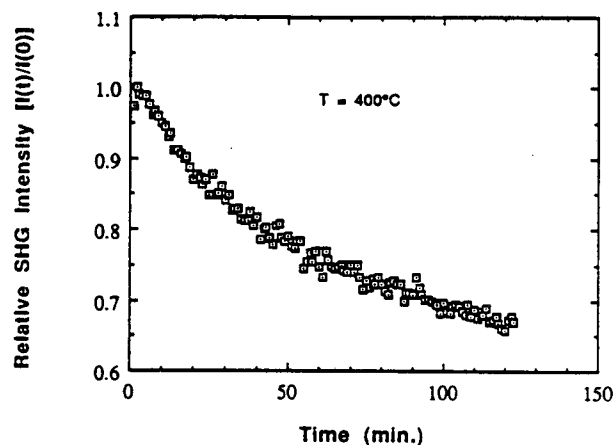


Figure 1 SHG versus time from a polyimide sample covered with an 8A Cu layer at 400°C . The sample was preheated to 350°C for 40 hours to remove Cu atoms and small Cu clusters from the sample surface via diffusion into the bulk.

By measuring the decay of SHG at different sample temperatures above T_g , we can obtain the temperature dependence of the diffusion coefficient of Cu clusters in polyimide. Figure 2 shows that an Arrhenius plot describes the diffusion coefficient versus temperature $T > T_g$ fairly well. Below T_g , the diffusion coefficient drops sharply. This indicates that diffusion of Cu clusters is much more prominent about T_g . Our SHG measurement below T_g could be complicated by competition between diffusion and aggregation.

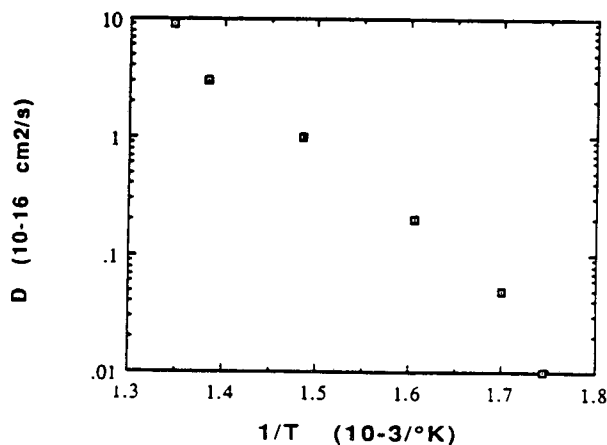


Figure 2 An Arrhenius plot of the diffusion coefficients of Cu clusters versus temperature. The glass transition temperature of the sample was $593 \pm 10^\circ\text{K}$.

As predicted by Faupel et. al. ¹⁴ in a three-dimensional Monte Carlo calculation, even with the deposition of only 1/4 monolayer of Cu on polyimide, there is already a tendency toward Cu cluster formation. A TEM measurement by LeGoues et. al. ¹³ showed that heating a Cu-covered polyimide to 523°K-573K or depositing Cu on a substrate at the same temperature range could lead to formation of Cu clusters with a typical size of 10^2 Å to 10^3 Å at the Cu/polyimide interface. SHG, via its enhancement on metal particles, allows us to monitor the cluster formation of Cu clusters. When the sample is at a temperature below T_g with more than a monolayer Cu deposited, the cluster formation of Cu on the surface dominates. In such a case, we actually found an increase of the SHG signal with time, as shown in Figure 3. A similar sample kept at room temperature gives a constant SHG signal. The increasing SHG can be attributed to the gathering of Cu particles to form larger Cu clusters leading to a larger enhancement of SHG. Such an effect is more significant when the Cu mass thickness on the polyimide is higher. For example, the enhancement for a sample with a mass thickness of 35Å was found to be about a factor of 7 at 575°K, while a thickness of 8Å only gave an enhancement of 1.5 under the same experimental conditions. This is presumably because the higher Cu mass thickness results in larger cluster size and hence stronger surface SHG enhancement. The presence of larger clusters was evidenced in our experiment by an obviously stronger light scattering from the rough surface.

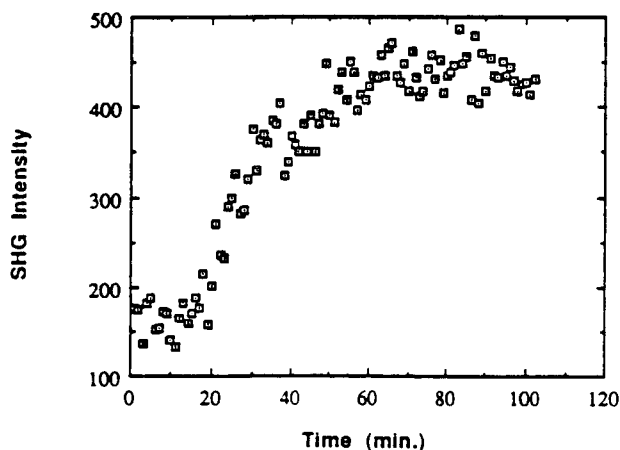


Figure 3 SHG as a function of time from a sample with 20Å of Cu on polyimide at a temperature 10°C below T_g . The increase in signal with time is presumably due to aggregation of Cu.

The existence of Cu clusters and their diffusion into polyimide can be seen in the following experiment. A Cu-covered polyimide sample was kept at a temperature just below T_g for a long time (120 min.). At the end of the storage, atoms and small clusters of Cu should have already diffused into polyimide, and only large clusters remained on the surface. Diffusion of large clusters into polyimide only became appreciable when the sample temperature was increased above T_g . The results are shown in Figure 4.

From the above experiments, we can glean some insight of Cu diffusion into polyimide. With Cu on polyimide, several processes generally occur: Diffusion of Cu atoms into polyimide is rather fast, but at sufficiently high temperature, Cu cluster formation on the surface can compete with it. Larger clusters are formed with higher mass thickness and at higher temperature ($T < T_g$). Diffusion into polyimide is slow for larger clusters. However, at temperature significantly higher than T_g , even large Cu clusters diffuse into polyimide fairly rapidly.

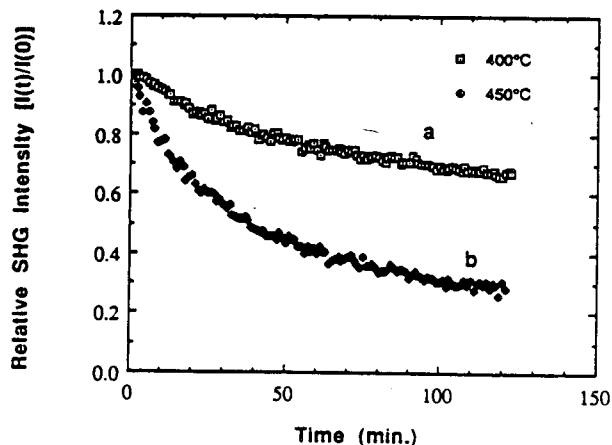


Figure 4 SHG variation with time (Curve a) from Cu-on-polyimide at 400°C without preheating the sample. Increasing the sample temperature to 450°C leads to an accelerated diffusion of Cu (curve b).

Diffusion of Cu into polyimide can be impeded by a buffer layer. A previous study by X-ray photoelectron spectroscopy (XPS) ²² showed a thin layer of Ti between Cu and polyimide can efficiently stop the Cu diffusion. We can probe in-situ such an effect by the SHG technique: a Ti layer with a mass thickness of 10 Å was deposited on the polyimide sample followed by a depositing of 10 Å of Cu. The SHG signal from the Cu/Ti/polyimide sample at different

temperatures was then measured. Figure 5a shows the time-dependent SHG at 400°C with a 10Å Ti. In comparison with the result of Cu/polyimide in Figure 1, the diffusion is obviously retarded by the Ti layer. When the Ti mass thickness was increased to 20Å, the effectiveness of the Ti layer as a diffusion buffer was even more obvious. As seen in Figs. 5b and c, the SH signal is practically independent of time even when the sample temperature was increased to 450°C, at which even the large Cu clusters would have diffused into polyimide rapidly without the Ti buffer layer. The results of Figure 5 conclusively demonstrate that one or two monolayers of Ti layer are sufficient for arresting Cu diffusion into polyimide.

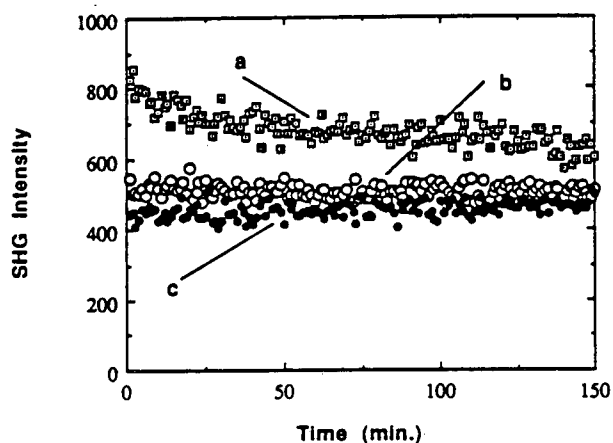


Figure 5 SHG versus time from Cu-Ti-polyimide samples with (a) 10Å Ti interfacial layer and $T=400^{\circ}\text{C}$; (b) 20Å Ti interfacial layer and $T=400^{\circ}\text{C}$; (c) 20Å Ti interfacial layer and $T=450^{\circ}\text{C}$. Comparison with result in Fig. 4 shows the effectiveness of Ti layer as a diffusion buffer.

The ability of Ti to form a buffer layer to prevent Cu from diffusion into PI is presumably due to the strong interaction between Ti and the polymer segments and between Ti and Cu. The imide moiety of polymer backbone and Ti can have a strong covalent interaction²³, while Ti and Cu can interact to form a Ti-Cu alloy. The strong binding of Cu on Ti makes the former immobile and hence the diffusion unlikely. For the same reason, the Ti layer acts as an adhesion promoter between Cu and PI.

In summary, we have demonstrated that the surface-sensitive SHG technique can be used to study in-situ the Cu cluster formation and diffusion into polyimide. The relevant diffusion coefficients can be measured. The effectiveness of a Ti buffer to impede Cu diffusion into polyimide has also been observed. One or two monolayers of Ti seem sufficient for stopping the diffusion.

Acknowledgment

Ms. Hui-ying Xu helped with the performance of the experiments. This work was supported by the Digital Equipment Corporation and the State of California MICRO Program with equipment borrowed from CAM of Lawrence Berkeley Laboratory. The constructive comments of S. C. Freilich, Gus Ouano, Solomon Beilin and Chung Ho are especially appreciated.

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