Radiation-induced interface phenomena: Decoration of high-energy density ion tracks

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The effect of 20 MeV Cl^{4+} ions incident on Au-SiO_2 and Ag-SiO_2 interfaces was investigated using high-resolution transmission electron microscopy. Cross-sectional micrographs expose beam-induced gold interfacial transport and migration into the SiO_2. No such migration was observed for silver films. The relevance of this phenomenon to the adhesion improvement found at corresponding irradiation doses is discussed.

When an energetic ion penetrates a solid, the mode of interaction with the surrounding material is determined by its specific energy. In the keV/amu region, energy is transferred mainly through elastic collisions with the target atoms (nuclear stopping). Above ~0.1 MeV/amu, however, ionization and excitation processes prevail (electronic stopping). If the supply and mobility of electrons in a material are low enough, such electronic effects may extend over times which are sufficient to allow for atomic displacements. Accordingly, electronically induced damage has only been observed in insulating materials and in some semiconductors. Despite the differences in primary interactions, the resulting effects are in some cases similar to those caused by nuclear stopping events. For example, substantial sputtering yields have been reported for dielectric surfaces due to high-energy ion impact.[1-4]

Griffith *et al.*[5] invoked these similarities in models to describe their observation that MeV ion irradiation produced adhesion enhancement of metal films deposited on insulators. However, substrates other than insulators were also investigated and, in general, bonding metal films to semiconductors and metals was found to be easier.[6] Different mechanisms seem to be associated with different systems. For metal-Teflon interfaces, radiation-induced toughening of the Teflon surface appears to be one of the crucial factors.[7,8] In bonding nonoxidizing metal films to oxides, the importance of interfacial mixing has been stressed.[9] Although numerous methods have been exploited in the search for the physical explanation of this phenomenon, the vast majority require a compromise between sensitivity, resolution, and the possibility of "reaching" the interface.

In this letter, we report on the use of cross-sectional imaging in transmission electron microscopy (XTEM). Gold thin films on silicon oxides were examined in our first attempt to visualize the effects of penetrating ions in the electronic stopping regime, and to correlate such effects with the accompanying adhesion enhancement. Certain properties of this system were expected to be advantageous in terms of providing distinctive results that are reasonably easy to interpret. First, a relatively high sputtering yield was previously reported for fused silica.[4] Second, stable Au-Si or Au-O compounds are generally not formed, the presence of which could inhibit any atomic mobility that might be initiated by the impinging ions. Finally, the irradiation parameters (ion species, specific energies, threshold doses, etc.) required for adhesion improvement are well established.[9] For comparison purposes, the Ag-SiO_2 system was also studied.

Wafers of (100) orientation silicon were cut into 25×50 mm^2 samples and etched in a HF:H_2O 1:50 solution for about half a minute. On some substrates, a thermal oxide of ~2000 Å thickness was subsequently grown by heat treatment at 1100 °C in an oxygen atmosphere. The samples were then loaded into an evaporation chamber working at a base pressure of 2×10^{-6} mbar. Gold and silver films were deposited to a thickness of 300 Å as monitored by a quartz crystal oscillator. Ion irradiation with 20 MeV Cl^{4+} to a dose of 10^{15} ions/cm^2 was carried out using the Uppsala EN-tandem Van de Graaff accelerator. This dose has been found to improve substantially the adhesion for the investigated systems.[9] A well-focused beam spot (<2 mm) was swept over half the sample area (25×25 mm^2) using an electrostatic raster scan system.[10] The beam current was kept at 80 nA/cm^2. Scotch Tape tests and scratch tests were used to establish whether any adhesion improvement had taken place.

XTEM analysis[11] of irradiated and nonirradiated areas was performed in a Philips 430 scanning transmission electron microscope operating at 300 kV. Cross sections were prepared by gluing two samples face to face and subsequently curing at 100 °C for about 1 h. The specimens were then mechanically polished to a thickness of ~10 μm. Finally, electron transparency was achieved by ion milling using 5 keV Ar^+ ions. During the last step, liquid nitrogen was employed to cool the samples, thereby reducing heating effects.

Figures 1(a) and 1(b) show XTEM micrographs of unirradiated and irradiated Au-SiO_2 interfaces, respectively. The pictures show a projection of ~1000-Å-thick specimens. At a radiation dose of 10^{15} ions/cm^2, transport of gold across the interface and further migration into the silicon oxide is clearly exhibited. The corresponding migration range is approximately 500 Å. Furthermore, high-resolution images revealed that a crystalline gold phase was formed in the oxide. In accordance with this result, adhesion tests showed a considerable increase in thin-film bonding. Although the penetration of film atoms is definitely radiation induced, it is not evident from the XTEM analysis whether

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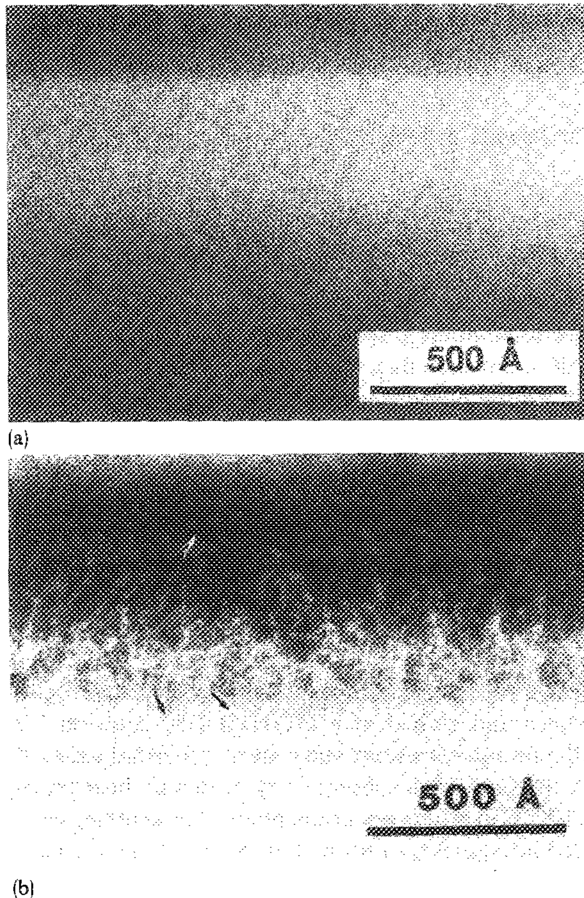

FIG. 1. Cross sections of the Au-SiO_2 interface (a) before and (b) after irradiation to 10^{15} ions/cm^2. Arrows indicate the range of Au migration.

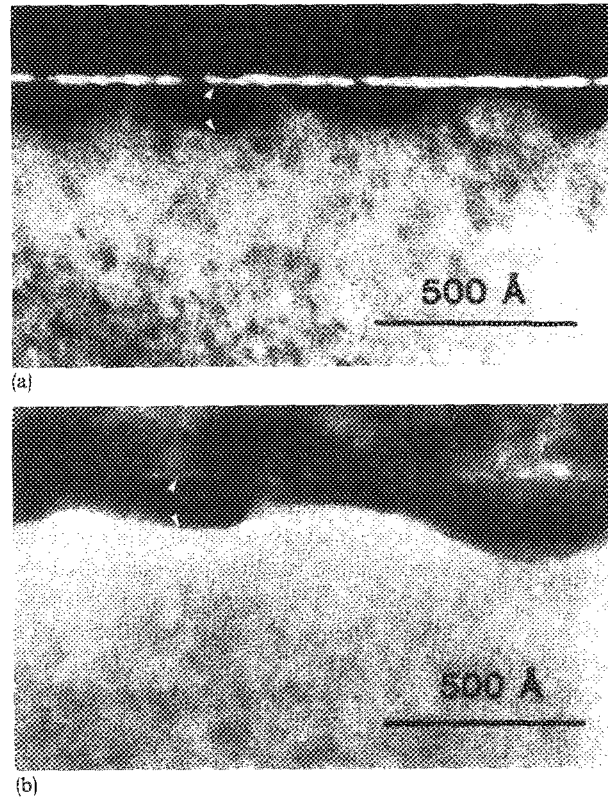

FIG. 2. XTEM micrographs of Au-Si interfaces with (a) thick irradiated (10^{15} ions/cm^2) and (b) thin unirradiated silicon native oxide. Arrows indicate the range of Au migration.

this is a result emanating entirely from the ion bombardment or if thermal effects are involved. Such effects might be accomplished either by macroscopic heating of the samples during the irradiation process, or by the curing required for preparing the cross sections.

When the oxide layer separating the gold and silicon was sufficiently thin for the migration range to exceed that of the oxide, gold was found to "leak" through the oxide and diffuse into the silicon substrate—again accompanied by a substantial increase in thin-film adhesion. In Fig. 2(a), this phenomenon is shown for an ~ 30-Å-thick silicon native oxide and a dose of 10^{15} ions/cm^2. The migration range is limited here to ~ 100 Å. The dynamic process associated with this result can be divided into two steps related to different effects: the transport of gold across the oxide and the diffusion of gold into the silicon. The first was not observed for unirradiated areas and, although the migration as such might be due to elevated temperature during ion bombardment or XTEM sample preparation, it evidently requires irradiation for its initiation. The second, which is purely a thermal effect, was also observed, both for irradiated and unirradiated [Figure 2(b)] areas, for samples[12] having an oxide thickness below ~ 10 Å. Incidentally, no detectable difference in adhesion was found in this case.

Since the micrographs presented above show a projection of the ~ 1000-Å-thick cross sections, one may conclude that the number of leaks produced in the oxide [seen as dark regions in Fig. 2(a)] is only a small fraction of the number of beam particles having penetrated the interface (10^{15} cm^{-2}). That is, an impinging ion does not usually generate enough damage in the oxide to allow for the migration of gold atoms. The observed phenomenon could therefore be attributed to the integrated effect resulting from overlapping ion tracks. Another possible interpretation may be derived from fluctuations in the ionization density along the path of a penetrating ion; hence, there is a certain probability that the number of ionizations within some volume would exceed the density required to cause sufficient modification of the interface. As the range of migration appears to depend strongly on the underlying substrate [cf. Figs. 1(b) and 2(a)], one may safely assume that the observed phenomena are not a direct effect of recoiling gold atoms.

The Ag-SiO_2 interface showed no mixing following ion irradiation. In view of previously reported comparisons between the Au-SiO_2 and Ag-SiO_2 systems, regarding thin-film adhesion,[6,9] this difference could be attributed to the ability of silver to oxidize. As oxygen constitutes the outermost layer of a SiO_2 surface, stable bonds may be formed between the silver and oxygen atoms as a result of the ionizing radiation and, therefore, no migration of silver should be expected. For native silicon oxides, the highest concentration of oxygen is to be found at the substrate surface and, accordingly, this system did not reveal any trace of mixing either.

The technique presented herein offers a new perspective for probing the mechanisms involved in radiation effects in

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solids. Not only can track damage be observed by amorphization of crystalline phases (e.g., quartz or sapphire) but also, if certain requirements are met, damaged regions can be mapped even in amorphous materials by allowing appropriate atomic species to migrate into the material under study. A similar technique was previously reported[13] using a phosphate glass containing silver in which preferential precipitation of silver along ion damaged regions was observed.

By tuning the oxide thickness, specific energy, ion dose, annealing temperature, etc., the present technique might be used for the controlled manufacturing of atomic leaks—large or small—in dielectric materials. Moreover, as the exhibited effects are remarkably consistent with changes in interfacial bond strength, further investigations may complement the existing knowledge in the field of radiation-induced adhesion enchancement.

In conclusion, we have presented a technique for recording track damage in amorphous materials. This was accomplished by MeV ion bombardment of Au-SiO_2 interfaces which resulted in atomic transport of gold across the interface and further migration into the damaged regions in the underlying silicon oxide layer. The inherency of phase contrast effects in XTEM, associated with such a migration, is manifested by cross-sectional mapping of the gold-decorated accumulated track damage. The observed effects, induced by the ion irradiation, are accompanied by an improvement in thin-film adhesion. In the case of radiation-induced adhesion of silver films to silicon oxides, however, no mixing was observed. This might be attributed to silver oxide compounds formed at the interface and inhibiting further migration of the silver atoms. The difference in behavior between gold and silver films, as revealed by XTEM, indicates that the adhesion improvement is associated with preferential bonding to silicon and oxygen, respectively, as suggested previously.[9] By varying the ion energy, radiation dose, beam current, and annealing temperature, a more exact origin of the present observations may be defined.

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