CONF-961202--6

SAND096-1681C
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# SEGREGATION OF COPPER TO (100) AND (111) SILICON SURFACES FROM INTERNAL $Cu_3Si$ PRECIPITATES

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## ABSTRACT

The energetics of copper segragation to silicon surfaces were examined by measuring the Cu coverage after equilibration between Cu on the surface and internal $Cu_3Si$, for which the Cu chemical potential is known. For oxide-free surfaces the Cu coverage was close to one monolayer on (111) surfaces but was much smaller on (100) surfaces. The Cu coverage was greatly reduced by oxide passivation of the surface. LEED showed the 7x7 structure of the clean (111) silicon surface converted to a quasiperiodic 5x5 structure after equilibrating with $Cu_3Si$. The 2x1 LEED patterns for (100) surfaces indicated no change in surface structure due to the $Cu_3Si$. These results show that the that the free energy of copper in $Cu_3Si$ is higher than that of copper on (111) surfaces but lower than that of copper on (100) surfaces.

## INTRODUCTION

Segregation of transition metal impurities to surfaces or interfaces can have detrimental or beneficial effects in silicon-based microelectronic devices. Controlled segregation of impurities to regions remote from device structures, i.e. gettering, is routinely used to prevent uncontrolled segregation to critical regions which may cause failure. Internal gettering is a widely used process in which oxide precipitates and associated lattice defects provide sites for precipitation of metal-silicide phases [1]. Segregation of impurities onto surfaces of internal microcavities has also been examined as a potetial gettering process [2,3]. It was observed that gettering to cavities can dissolve pre-existing internal metal silicide precipitates of Cu, Au and Ni [3]. This transfer of metal from silicide to cavities occurs via the solution state and is driven by a lower chemical potential for the metal at cavities than in the silicide phase. A lower chemical potential implies that gettering by cavities should be capable of reducing concentrations of mobile impurities to lower levels than can be achieved by conventional internal gettering. Measurements and modeling of impurity redistribution between cavities and silicide have yielded values for the free energy of binding to cavities and for coverages after equilibration with silicide for several metals [3]. However, these results are averages over the differently oriented facets of the cavities [2,4].

Here we examine the energetics of Cu segregation onto external surfaces of Si where the orientation is known. This study differs from the many previous studies of copper evaporated onto silicon surfaces in that here we measure the surface coverage of Cu after equilibration at elevated temperatures with pre-existing internal $\eta$-$Cu_3Si$ precipitates.

## EXPERIMENTAL METHOD

The basic method in these experiments was to prepare clean ordered surfaces by thermal desorption of a thin oxide from (100) and (111) surfaces [5], or hydrogen from (111) surfaces [6], then anneal the samples to allow copper on the clean surface to come into thermodynamic

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equilibrium with internal silicide. After equilibrating, the samples were rapidly cooled to preserve the equilibrium copper coverage on the surface, and then analyzed.

The surface copper coverage was measured by Rutherford backscattering (RBS). Auger electron spectroscopy (AES) was used to indicate the presence of oxygen, carbon and copper on the surface. The atomic structure of the surface was monitored using low energy electron diffraction (LEED). The samples were radiatively heated by a tungsten filament behind the sample, and the sample temperature was measured by an infrared thermometer viewing the front of the sample.

Samples were (100) and (111) oriented float zone silicon 250μm thick with a resistivity > 1 kΩ cm. Samples were chemically cleaned leaving a thin chemical oxide using the procedure described by Ishizaka and Shiraki [5]. In addition, some (111) samples were prepared with hydrogen terminated surfaces by rinsing in $NH_4F$ [6]. After chemical cleaning the samples were implanted with copper on one side at 150 keV to a fluence of 1000 Cu/nm$^2$. This implant produced a peak Cu concentration of 10 atomic % about 100 nm beneath the surface. Transmission electron microscopy has shown that the η-$Cu_3Si$ equilibrium silicide phase is formed by annealing at 600°C [2,7]. Directly after the Cu implant the samples were transferred into a UHV chamber for analysis of the side not implanted with copper.

Samples were first heated to 750°C for ten minutes, then cooled to room temperature and analyzed. They were then heated to 850°C for 10 minutes, cooled and analyzed again. The heating has three important effects. First, it insures that the implanted Cu is in the equilibrium η-$Cu_3Si$ phase [2,7]. Second, it establishes thermodynamic equilibrium between copper in the silicide, copper in solution and copper bound to the front surface of the sample. Finally, heating to 750°C desorbs hydrogen from the hydrogen terminated (111) surfaces [6]. The thin chemical oxide is desorbed from the oxide terminated surfaces by heating to 850°C, but not by heating to 750°C [5]. These procedures for preparing clean well-ordered surfaces were tested using samples which were not implanted with copper. H terminated Si(111) surfaces had sharp 1x1 LEED patterns before heating and 7x7 LEED patterns after heating to 750°C or higher. AES on the oxide terminated surfaces showed a large peak from oxygen which was unchanged after heating to 750°C but was entirely absent after heating to 850°C. LEED showed sharp 2x1 and 7x7 patterns for the (100) and (111) surfaces, respectively, after heating the oxide terminated surfaces to 850°C. These tests confirmed that without copper, (100) and (111) samples prepared with oxide terminated surfaces have clean ordered (2x1) and (7x7) surfaces, respectively, after heating to 850°C, but still have oxide terminated surfaces after heating to 750°C. Samples prepared with H terminated (111) surfaces had clean ordered (7x7) surfaces after heating to 750°C or higher.

The annealing time of ten minutes was chosen to be much longer than the time to reach equilibrium between Cu on the front surface and the silicide near the back surface. Equilibrium is reached by diffusion of Cu through the silicon lattice from the silicide to the front surface. The equilibration time was determined by solving the diffusion equation with saturable traps at the front surface and with the concentration at the back fixed at the solid solubility. Using published values for the diffusivity and solubility [2,8], equilibration times are estimated to be about 10 seconds at 850°C and 90 seconds at 750°C.

The cooling rate at the end of the anneal was sufficiently fast to retain the copper coverage on the front surface present during the anneal. The initial cooling rate was measured by the IR thermometer to be ~ 100°C/sec. This is close to the rate expected for cooling by radiative heat loss.

EXPERIMENTAL RESULTS

The coverage of copper on the front surface was measured by RBS using an analysis beam of 1 MeV $^4$He. The samples were aligned with the analysis beam for axial channeling to reduce scattering from the silicon. Table 1 gives the main results from the RBS measurements on (100) and (111) samples prepared with oxide terminated surfaces, denoted by (100)-O and (111)-O respectively, and on (111) samples prepared with H terminated surfaces, denoted by (111)-H. The experimental uncertainty indicated in table 1 is the relative uncertainty due to the counting statistics. In addition, there is a systematic uncertainty of about ± 10% in the absolute values of copper coverages from RBS.

Samples prepared with oxide terminated (100) and (111) surfaces have much more Cu after annealing at 850°C than after annealing at 750°C. This shows that the coverage of copper is greatly reduced by the surface oxide, which is still present after heating to 750°C but absent after heating to 850°C. This conclusion is reinforced by comparing the Cu coverage on the (111) samples after heating to 750°C, which desorbs the H but not the oxide. Again the oxide terminated surface has much less Cu than the oxide free surface.

The Cu coverage also depends strongly on the surface orientation. After annealing to 850°C the areal density of Cu is about five times higher on (111) surfaces than on (100) surfaces. Dividing the measured Cu areal density by the Si atom areal density (6.8/nm$^2$ for (100) and 7.8/nm$^2$ for (111) surfaces) gives Cu coverages of 1.6 monolayer (ML) on (111) surfaces and 0.35 ML on (100) surfaces after annealing at 850°C.

The copper can also be seen in the AES spectra. Figure 1 shows AES spectra for (111) and (100) surfaces after annealing at 850°C. Spectra are shown for samples both with and without internal silicide. (111) samples with Cu have a Cu $M_{23}VV$ Auger peak at 60 eV which is absent in samples not implanted with Cu, whereas the Cu Auger peak is much smaller for Cu implanted (100) samples. The Cu Auger peak was not present on (100) or (111) samples prepared with oxide terminated surfaces after heating to 750°C, i.e. which still had oxide terminated surfaces after the anneal. The Cu Auger peak for Cu implanted H terminated (111) samples, after annealing at 750°C or 850°C, was the same as for Cu implanted (111)-O samples after the 850°C anneal. The conclusions from the Auger analysis are qualitatively the same as those from the RBS analysis. In particular, for oxide-free surfaces there is much more Cu on (111) surfaces than on (100) surfaces, and there is much less Cu on oxide terminated surfaces than on oxide-free surfaces.

The surface structure was determined by LEED. Figure 2 shows LEED images from (100) and (111) samples prepared with oxide terminated surfaces both with and without internal silicide. The LEED images in figure 2 were recorded on samples near room temperature after annealing at 850°C which desorbs the oxide. (100) samples show the same (2x1) LEED pattern from the dimer reconstruction both with and without silicide. (111) samples without silicide had (7x7) LEED patterns whereas (111) samples implanted with Cu showed a very different LEED pattern with an apparent 5x5 periodicity. (111) samples prepared with H terminated surfaces instead of oxide terminated surfaces gave the same LEED patterns after annealing at 750°C or 850°C as those shown in figure 2, i.e. 7x7 patterns without silicide and 5x5 patterns with silicide. The LEED results show that for surfaces free of oxide, (100) surfaces are unchanged by the presence of internal silicide, whereas (111) surfaces are changed from the (7x7) to a (5x5) structure after annealing to equilibrate copper on the surface with the internal silicide.

## DISCUSSION AND CONCLUSIONS

The structure of copper evaporated onto silicon surfaces has been the subject of many studies [9-17]. The conclusions can be summarized as follows. Copper deposited onto Si(111) surfaces at temperatures between 200°C and 650°C forms an ordered two dimensional (2D) phase which saturates at a copper coverage of 1.3 monolayer when the layer completely covers the surface [9-12]. At higher coverages 3D islands of $\eta''$-$Cu_3Si$ grow on the surface while the surface between the islands remains covered by the 2D phase [9,10]. This 2D layer has a complex quasiperiodic structure which has been elucidated by X-ray standing wave [11], helium diffraction [13] and scanning tunneling microscopy [14,15] studies. Copper deposited onto Si(100) surfaces at temperatures above 130°C condenses into 3D islands of $Cu_3Si$ with the silicon surface between the islands unchanged and free of copper [12,17].

The ordered 2D phase on (111) surfaces gives the 5x5 LEED pattern [12] as we observed, and Auger electron spectra very similar to those we observed [10]. The Cu coverage on (111) surfaces equilibrated with internal $Cu_3Si$ which we measured (table I) is close to the value previously reported for full coverage by the quasiperiodic 2D phase. Our measurements of the copper coverage on surfaces after equilibration with internal $Cu_3Si$, and the previously reported studies of copper deposited onto silicon surfaces, both lead to the conclusion that the free energy of copper in $Cu_3Si$ is higher than that of copper on (111) surfaces but lower than that of copper on (100) surfaces.

Segregation of copper and other impurities onto surfaces of internal microcavities has been investigated as a potential gettering mechanism [2,3]. It was observed that gettering to cavities dissolved pre-existing internal $Cu_3Si$ precipitates at 450°C and 600°C [3]. This transfer of copper from silicide to cavities occurs via the solution state and is driven by a lower chemical potential for the copper at cavities than in the silicide phase. Measurements and modeling of impurity redistribution between cavities and internal silicide give a value for the free energy of copper bound to cavities which is about 0.8 eV/atom below that of copper in $Cu_3Si$ at 630°C [3]. With this strong binding, the copper at the cavities after equilibration with silicide should be saturated at the equilibration temperatures used in our study. In the cavity experiments the saturation coverage of copper was estimated to be 6.5 Cu/nm$^2$ from the areal density of copper measured by RBS, and measurements of total cavity surface area from transmission electron microscopy (TEM) [3]. The results from our investigation suggest that gettering of Cu at cavities may be mainly on the {111} facets. The saturation coverage found in the study of copper gettering at cavities is consistent with the coverage we observe on external (111) surfaces over approximately half of the cavity surface area. This is consistent with TEM which showed that the cavities were faceted with predominately {111} faces [2,4].

## ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy under contract DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy.

TABLE I. The coverage of copper on the front surface measured after annealing by RBS.

| Surface | 750°C Anneal (Atoms/nm$^2$) | 850°C Anneal (Atoms/nm$^2$) |
|---|---|---|
| (111)-H | $9.9 \pm 0.3$ | $12.2 \pm 0.4$ |
| (111)-O | $1.0 \pm 0.2$ | $12.3 \pm 0.4$ |
| (100)-O | $0.4 \pm 0.2$ | $2.4 \pm 0.2$ |

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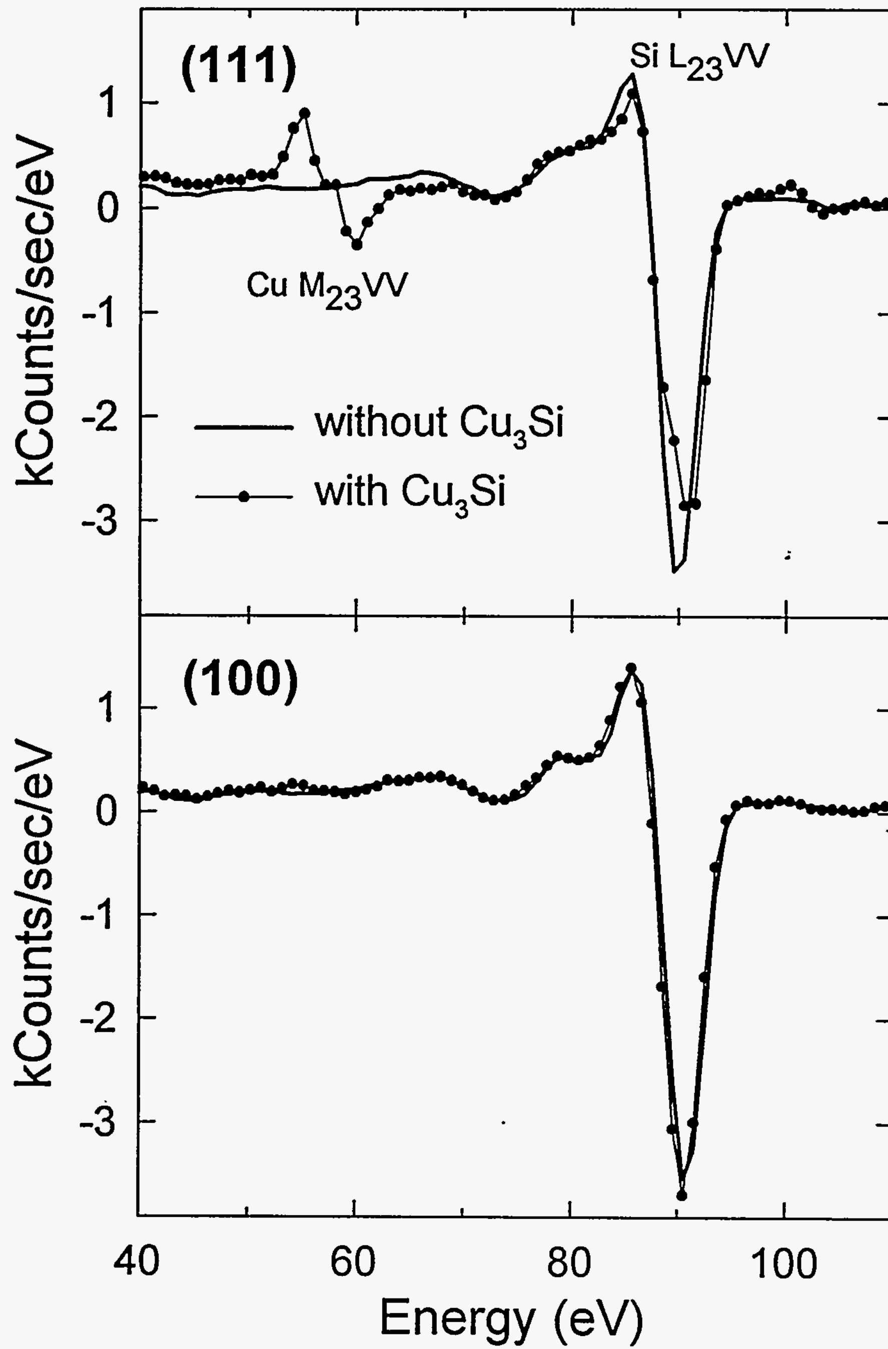


Fig. 1. Auger electron spectra on oxide free surfaces after annealing at 850°C, for (111) (above) and (100) (below) surfaces in samples with (dotted line) and without (solid line) implanted copper.

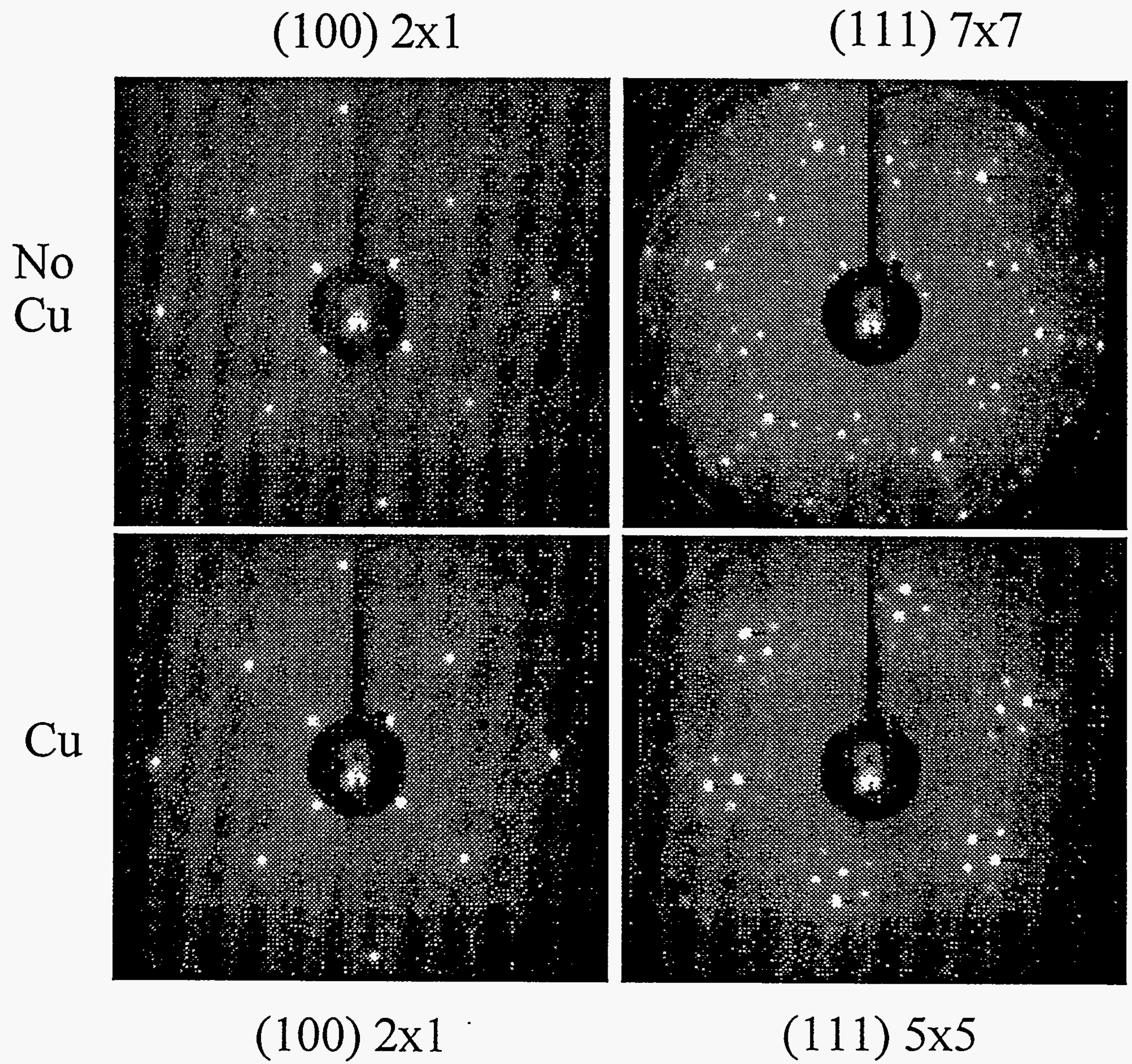


Fig. 2. LEED images on oxide free surfaces after annealing at 850°C, for (100) (left) and (111) (right) surfaces in samples with (below) and without (above) implanted copper.