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Reaction of nanometer-sized Cu particles with a SiO_2 substrate

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The thermal stability of nanometer-sized Cu particles on a 400–500 nm thick SiO_2 layer on top of a Si(100) substrate was studied after annealing in ultrahigh vacuum up to 620 °C. Atomic force microscopy, low-energy ion scattering, Rutherford backscattering spectrometry, and Auger electron spectroscopy measurements clearly show that Cu-silicide islands are formed. A direct reaction of Cu with the SiO_2 support is assumed, which is facilitated by a fairly strong metal-support interaction and by the wetting behavior of the silicide islands. Exposure to air at room temperature results in regeneration of the annealed Cu/SiO_2 system. © *1999 American Institute of Physics.* [S0003-6951(99)03120-4]

The interaction between metals and oxides is of great interest in studies of ceramic materials, semiconductor devices, and heterogeneous metal catalysts. Contact metallization processes are studied extensively due to the continued shrinkage of device dimensions in silicon integrated circuits.[1] Small metal particles dispersed over an (oxidic) support provide catalytical activity in chemical reactions and the metal-support interaction can dramatically affect the catalytical activity and selectivity.[2]

In this letter, we describe the interaction between nanometer-sized Cu particles and a flat SiO_2 substrate during annealing in ultrahigh vacuum (UHV). This system serves as a model catalyst to provide detailed information on surface and interface phenomena such as sintering, wetting, metal sublimation, encapsulation of the metal particles by the support, metal interdiffusion, and reaction of the metal with the support.[3,4] Supported Cu catalysts are applied in, e.g., the water-gas shift reaction and methanol synthesis.[5] Cu is also of great importance in the microelectronics industry, especially since the recent introduction by IBM of a new technology using Cu wires to link transistors in chips.[6,7]

The interaction between Cu and SiO_2 is generally believed to be rather weak.[8,9] Here we present the evidence for the formation of Cu-silicide islands during annealing in UHV up to 620 °C from the reaction of a SiO_2 substrate with fairly strongly attached Cu particles.

The wet-chemical preparation and characterization of our Cu/SiO_2 system have been extensively described in Ref. 3. Briefly, the SiO_2 substrates are Si(100) wafers with a 394 or 482 nm thick SiO_2 layer, prepared by a 1000 °C wet oxidation for 1–5 h. Cu is deposited by spin coating of a Cu-acetate precursor solution, followed by calcination in air at 450 °C, which produces homogeneously distributed Cu-oxide particles. Metallic Cu particles with an average height of 8 nm and covering approximately 2% of the substrate are obtained by reduction in hydrogen at 250 °C in the prechamber of an UHV setup. This preparation procedure does not affect the state of the SiO_2 substrate. The Cu–SiO_2 interaction after annealing in UHV was studied using low-energy ion scattering (LEIS), UHV atomic force microscopy (UHV-AFM), Rutherford backscattering spectrometry (RBS), and Auger electron spectroscopy (AES), each of these techniques in separate setups. Experimental details of AFM, LEIS, RBS, and AES measurements are described in Refs. 3 and 4.

LEIS experiments, which provide information about the composition of the outermost atomic layer, of the Cu/SiO_2 system initially show a slight increase in the Cu signal after UHV annealing prior to a rapid reduction in the Cu signal at temperatures above 350 °C. At approximately 620 °C, hardly any Cu signal could be discerned above the background noise. The Si and O signals do not change significantly as a function of annealing temperature. The signals are measured while keeping the sample at the annealing temperature for 10–15 min. Cu becomes fully visible again in LEIS spectra after sputtering at room temperature, using approximately 10^{16} He^+ ions/cm^2, indicating that Cu is present just below the surface of the sample after UHV annealing. RBS spectra before and after annealing up to 620 °C are identical within experimental error. The metal loading obtained from RBS is $1.5 \pm 0.1 \times 10^{15}$ Cu atoms/cm^2. Figure 1 shows AFM topography images before and after UHV annealing up to 620 °C. It has to be noted that the particle diameter in AFM images of nanometer-sized particles [Fig. 1(a)] is generally larger than the real diameter due to the tip-particle convolution.[10] Features of much larger dimensions are visible after annealing [Fig. 1(b)]. In addition, the frictional force (at a constant applied load) between the AFM tip and these features is smaller than the friction between the tip and the support, as opposed to the friction on the Cu particles before annealing which is larger than the friction on the support. The number density of the features observed after annealing is the same within experimental error as the Cu-particle number density before annealing.

These results may be explained by silicide formation, since it is known that the outermost atomic layer of Cu sili-

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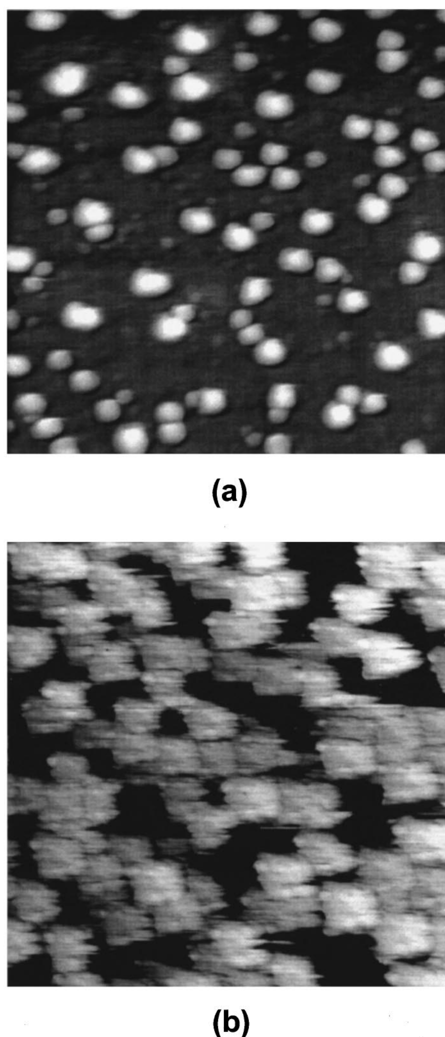

FIG. 1. UHV-AFM topography images (500×500 nm) of a Cu/SiO_2 sample (a) before annealing and (b) after UHV annealing up to 620 °C. The corresponding frictional force images (not shown) exhibit an inversion of contrast before and after annealing. After the experiments on the annealed samples, new samples with Cu particles were scanned, using the same tip, and AFM images similar to image (a) were obtained. This observation excludes that the features in image (b) are caused by a change in the shape of the AFM tip.

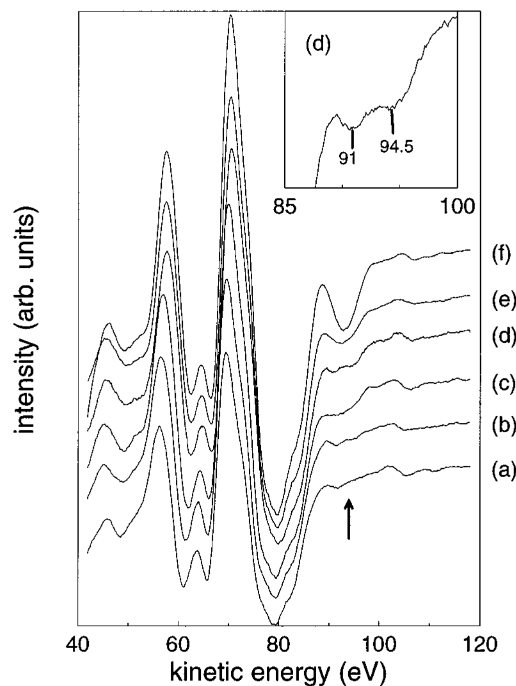

FIG. 2. AES results of a Cu/SiO_2 sample, using an 8 keV electron beam with a spot size of approximately 50 μm and a beam current of 15 nA. Differential AES spectra of the Si *LVV* region are shown (a) before UHV annealing, and during UHV annealing (b) at 320 °C, (c) at 500 °C, (d) at 620 °C for 10 min, (e) at 620 °C for 30 min, and (f) at 620 °C for 2 h. The inset shows the Si (92 eV) peak splitting for (d), indicating the formation of Cu silicide.

cide is strongly enriched in Si.[11,12] Also encapsulation of the Cu particles by the support may be the reason for the disappearance of Cu from the topmost surface layer. However, the observation of a difference in frictional force between the tip particle and tip support in AFM after UHV annealing is in disagreement with the latter mechanism and strongly indicates the formation of a new compound (silicide) after annealing.

In order to find more evidence for Cu-silicide formation after annealing, AES measurements have been performed. Cu silicide can be distinguished by the splitting of the Si *LVV* peak at 92 eV into two peaks at 90 and 94 eV.[13,14] In Fig. 2, AES spectra of the Si *LVV* region of our Cu/SiO_2 system are presented after various treatments. We will concentrate on the Si region, since no significant changes are expected and observed for the Cu *LMM* region after annealing. The AES spectrum before annealing [Fig. 2(a)] does not show a peak at 92 eV, since SiO_2 only results in Si peaks at 63, 67, and 80 eV, and the Si substrate is not visible by AES because it is covered by the thick SiO_2 layer. During annealing in UHV, a peak at approximately 92 eV starts to grow with increasing annealing temperature and time. A closer look at the spectrum measured at 620 °C, after the sample was held at this temperature for 10 min [Fig. 2(d)], reveals a splitting of the 92 eV peak into two peaks at 91 and 94.5 eV. After prolonged annealing at 620 °C, the peak splitting disappears which can be attributed to additional Si segregation to the topmost surface layer. These results are in good agreement with AES measurements on bulk Cu silicides by Frank and Falconer.[13] AES measurements were repeated during UHV annealing of a SiO_2 substrate without Cu particles. Only a weak signal at 92 eV could be discerned, which may be attributed to a small amount of Si formed by the reduction of SiO_2 by the electron beam.[15] From these AES measurements, we conclude that Cu-silicide formation takes place during annealing of the Cu/SiO_2 sample in UHV.

We have also studied the stability of the Cu-silicide particles. LEIS experiments do not show a significant change after cooling down to room temperature, while AES measurements show that the peak at 92 eV slowly disappears until it has almost completely vanished after keeping the sample for 16 h in UHV at room temperature. Exposure of the annealed samples to air at room temperature shows more remarkable changes. After 2 h of exposure to air, Cu is clearly detected again by LEIS. The Cu signal grows with increasing exposure time and becomes even two to four times larger than before UHV annealing after more than 37 h. AFM shows that after 2 h of exposure to air, particles are visible exhibiting similar dimensions and a similar particle number density as before annealing, but the interaction be-

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tween the AFM tip and a particle is still somewhat different than before annealing. After a few days of exposure to air, the tip-particle interaction was similar to that before annealing. These results show that annealed Cu/SiO_2 samples can be regenerated by exposure to air at room temperature.

It is known for metal silicides that silicon oxidizes much more rapidly in air than does pure Si.[13,14,16] Room-temperature oxidation of Si is catalyzed by Cu_3Si and a thick amorphous SiO_2 layer grows spontaneously beneath the Cu-rich layer.[17,18] So the ease of regeneration of the annealed Cu/SiO_2 samples as described above can be understood from the oxidation behavior of a silicide and is another piece of evidence for the presence of Cu silicide after annealing in UHV.

We believe that Cu silicide is formed by a reaction of the Cu particles with the 400–500 nm SiO_2 top layer, in contrast to the prediction by Pretorius *et al.*[9] that a reaction between Cu and SiO_2 cannot occur using simple thermodynamical arguments, and that the Si substrate is not involved in the silicide formation. There is no driving force for Si to diffuse through the SiO_2 layer to react with Cu at the surface, illustrated by the fact that the growth and decomposition reactions of a SiO_2 layer on Si proceed at the SiO_2/Si interface and that Si is the immobile species.[19,20] If the SiO_2 layer is not thick enough, the direct reaction between Cu and SiO_2 may compete with Cu diffusion through the SiO_2 layer to the SiO_2/Si interface where silicide is formed, as described by Dallaporta *et al.*[21] For Cu particles on a 5 nm SiO_2 layer on top of a Si(100) wafer, we have clearly observed Cu interdiffusion in the Si substrate after UHV annealing up to 620 °C.[4]

Due to the wet-chemical preparation, Cu is fairly strongly attached to SiO_2 since no sintering of the Cu particles is observed during UHV annealing, and we believe that the silicide formation starts at the metal-support interface. Strongly bonded Cu may catalyze the Si–O bond breaking, since Cu also catalyzes the reverse reactions of Si–O formation.[13,14,16–18] Metal evaporation as applied by others[9,21] may result in a weaker metal-support interaction[4] and, therefore, not result in a reaction between Cu and SiO_2 during UHV annealing. We note that also impurities on the sample surface or constituents of the residual gas may help to reduce SiO_2.[22]

Furthermore, a new surface and interface are formed during silicide formation, so a thermodynamical model of silicide formation must include a change in surface and interface free energies. Such changes have not been taken into account by Pretorius *et al.*[9] Data of the interfacial energies are hardly available. Considering the surface free energies, it is energetically favorable for a Cu surface to convert into a Cu-silicide surface which is strongly enriched in Si. The influence of changes in surface and interface energies on the course of the reaction may be even more pronounced when the surface and interface areas increase by spreading the silicide compound over the support. Although the tip-particle convolution in AFM experiments does not allow an exact determination of the size of the metallic Cu particles and the Cu-silicide islands,[10] an increase in area of the Cu species after UHV annealing by a factor of approximately 5–10 can be derived[3] from Fig. 1. The spreading of Cu-silicide islands is also indicated by LEIS measurements after regeneration of the Cu model catalysts. If the Cu-silicide islands are exposed to air at room temperature, the Cu signal grows to a value which is approximately two to four times larger than before UHV annealing. Such wetting behavior has also been observed in the formation of other metal-silicide islands.[23,24]

In summary, strong evidence was found for silicide formation from the reaction of a SiO_2 substrate with fairly strong attached Cu particles after annealing in UHV up to 620 °C. The initial metal-support interaction and the wetting behavior of the silicide islands are of importance to facilitate the reaction between Cu and SiO_2.

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