Low energy ion beam modification of Cu/Ni/Si(100) surface

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Abstract. Cu/Ni bilayer has been prepared by thermal evaporation of pure Cu and Ni metals onto Si(100) surface in high vacuum; it was sputtered using argon ion beam in ultra-high vacuum. The ion beam-induced surface and interface modification was investigated using X-ray photoelectron spectroscopy and atomic force microscopy techniques. The deposited sample exhibits the formation of CuO nano-structures of size 40 nm on Cu surface and after sputtering with argon ion beam at a fluence of 5×10^{15} ions/cm², the surface exhibits a mound structure with an average size of about 100 nm. Interestingly, with sputtering at higher fluence of 2.4×10^{16} ions/cm², the surface exhibits broad pits of sizes ranging from 100 to 300 nm with an average depth of 10 nm. Bottom surface of these pits contains Ni atoms. The Cu 2p_{3/2} peak exhibits a shift of 0.3 eV towards high binding energy and also a large asymmetry of 0.11 after sputtering at high fluence compared with pure copper. These changes are attributed to Cu–Ni interactions at the interface.

Keywords. X-ray photoelectron spectroscopy; atomic force microscopy; ion beam sputtering; thin films; thermal evaporation.

1. Introduction

Metallic multilayers are extensively used in industries and basic science because of their novel physical and engineering properties. Metallic multilayers exhibit improved electronic, magnetic and mechanical properties (Osaka 2000; Sulitanu 2002; Ghosh *et al* 2007) compared with the pure metal constituents. Metallic multilayers find applications in magnetic heads and disks and also in microelectromechanical systems (MEMS). Copper is extensively used in electronics industry as an inter-connecting material because of its unique properties like high electrical and thermal conductivities. Copper inter-diffuses into Si and causes the deterioration of p–n junctions used in electronic devices. Such interdiffusion of copper is prevented by nickel diffusion barrier (Sun *et al* 1981; Lefakis *et al* 1983; Abdul-Lettif 2002). Cu/Ni layers are used in microactuators, nanomold for nanoprinting and magnetic devices (Lim *et al* 2004; Serre *et al* 2005; Alper *et al* 2007; Ghosh *et al* 2007). Magnetic multilayers have been recently investigated because of their numerous applications in industries and also because of challenges they offer in basic science (Gradmann 1986; Shin 1993; Lee *et al* 2004). CuNi alloys have good durability in seawater and are used in desalination technology (Hodgekiess and Vassiliou 2005).

Ion irradiation changes the physical and chemical properties of materials. Low energy inert gas ion bombardment introduces morphological and electronic changes on surface

or near surface region of materials (Karmakar and Ghose 2004; Medicherla *et al* 2010). Ion beam sputtering is widely used for surface patterning, surface cleaning and depth profiling of materials used for industrial applications as well as for basic science research (Chiang *et al* 1986; Polman 1997).

In this paper, we report the Ar ion bombardment-induced electronic and morphological changes occurring in Cu/Ni bilayer deposited onto Si(100) by thermal evaporation method in high vacuum. Core levels of the bilayer have been studied using X-ray photoelectron spectroscopy (XPS) technique and the surface morphology was investigated using atomic force microscopy (AFM) technique.

2. Experimental

Cu/Ni thin films were deposited onto Si(100) substrate using thermal evaporation of 99.99% pure Cu and Ni metals in a high vacuum of 2.0×10^{-5} mbar. The vacuum system was pumped by a diffusion pump and then the liquid nitrogen trap was filled up to reduce impurities from the deposition chamber. Prior to the deposition, Si substrate was degassed for a few hours in vacuum chamber to remove the surface contamination. Initially, a Ni layer of 40 nm was deposited onto clean Si surface and then a Cu layer of 20 nm was deposited on top of the Ni layer.

Sputtering and XPS measurements were carried out using a VG ESCA machine equipped with an argon sputter gun, twin anode X-ray source and a hemispherical analyser. Sputtering was carried out using a 3 keV argon ion beam in-situ

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in the preparation chamber at a base vacuum of 2.0×10^{-8} mbar. Argon ion current was fixed at $10 \mu\text{A}$ using an argon pressure of 5.0×10^{-6} mbar. Angle of incidence of the argon ion beam on the sample surface is about 15° measured from the surface normal of the sample. Sputtering was carried out in a de-focussed mode with a large spot size to cover the entire sample. The uniformity of sputtering was assured by observing the XPS signals at different positions of the sample and it was found that the line profile of Cu $2p$ remains the same. Samples have been sputtered for 10, 20 and 40 min for which the ion fluences are given by 6.0×10^{15} , 1.2×10^{16} and 2.4×10^{16} ions/cm², respectively. The samples have been transferred to the analysis chamber having a base vacuum of 2.0×10^{-10} mbar, immediately after sputtering, for XPS measurements. Cu $2p$ and Ni $2p$ core levels were measured at each sputtering time. The total resolution of the spectrometer is 0.8 eV measured as the full-width at half-maximum (FWHM) of $3d_{5/2}$ peak of clean silver. Binding energy (BE) was calibrated using Au $4f_{7/2}$ at 83.96 eV. The surface morphology was studied by AFM (Nanoscope III, Veeco) in tapping mode using a SiN tip (dimension 5–10 nm) immediately after taking out the samples from XPS chamber.

3. Results

Figure 1(a) shows the evolution of Cu $2p$ core level of Cu/Ni bilayer sputtered by argon ion beam with sputtering times as indicated in the figure. The spectrum of unsputtered sample is also shown for reference which exhibits four broad features corresponding to main lines ($2p_{3/2}$ and $2p_{1/2}$ and satellites as indicated in the figure). The observed satellite structure suggests that the unsputtered sample surface contains CuO layer on top of the Cu surface. It is clearly evident that the Cu $2p_{3/2}$ peak splits into two. Such splitting is not apparent in the Cu $2p_{1/2}$ peak because of low intensity and the increased width of $2p_{1/2}$ compared with $2p_{3/2}$ is because of Coster–Cronig transitions. After sputtering the satellites disappear and main lines become sharp, indicating pure metals without oxides. Some amount of oxygen is expected in the bulk of the film as the deposition carried out at 2.0×10^{-5} mbar pressure. In this case deposition was carried out by quickly evaporating large amount of metal. As per the geometry of the vacuum system used for deposition, only a minute fraction of the evaporated metal goes to the substrate and the rest is deposited on the walls of the chamber. Therefore, most of the residual oxygen in the chamber is taken away by the metal deposited on the walls, reducing the oxide formation in the film deposited on the substrate. Within the detection limit of the XPS system, we did not observe oxide formation in the bulk of the film in Cu $2p$ or Ni $2p$ core levels. The Ni $2p$ core level is observed only after sputtering the sample for 40 min and is shown Figure 1(b). Ni $2p_{3/2}$ occurs at a binding energy of 853.0 eV with a spin orbit splitting of 17.5 eV.

Figure 2(a) shows the Cu $2p_{3/2}$ peak of Cu/Ni/Si(100) after sputtering for 10, 20 and 40 min along with the

Figure 1. (a) Cu $2p$ spectra of as deposited and sputtered Cu/Ni/Si(100) and (b) Ni $2p$ spectrum of Cu/Ni/Si(100) after 40 min sputtering.

numerically fitted curves. These spectra have been fitted using Doniach–Šunjić line shape convoluted with a Gaussian function of width 0.8 eV to take care of the experimental broadening. The Lorentzian Width (LW) and the asymmetry parameter obtained from fitting for 10 min sputtered sample are 0.45 eV and 0.07, respectively. After sputtering for 20 min, the Cu $2p_{3/2}$ peak shifts to higher binding energy by 0.1 eV. The LW and asymmetry parameter were found to be the same as those of 10 min sputtered sample. Interestingly, the Cu $2p_{3/2}$ peak shifts to higher binding energy by 0.3 eV and the LW and peak asymmetry increase to 0.49 eV and 0.11, respectively. Figure 2(b) shows the Cu $2p_{3/2}$ peak of unsputtered sample. This spectrum has been deconvoluted into four peaks as shown in the figure. The two main peaks at 932.4 and 934.7 eV correspond to pure Cu metal and CuO, respectively. The low intense features at 940.7 and 943.7 eV correspond to the satellites belonging to CuO. The binding energy of $2p_{3/2}$ for CuO is 0.9 eV higher compared with the value reported for bulk CuO (Kotani *et al* 1990). This discrepancy can be attributed to the two-dimensional nature of the surface oxide. The main line of Cu $2p_{3/2}$ observed at 934.7 eV for CuO occurs due to $2\bar{p}_3d^{10}\bar{L}$ configuration where $2\bar{p}$

Figure 2. (a) Cu $2p_{3/2}$ spectra of Cu/Ni/Si(100) sputtered for (1) 10 min, (2) 20 min and (3) 40 min. Dots represent the experimental data and the solid line indicates the numerically fitted Doniach–Šunjić line shape in each case. (b) Cu $2p_{3/2}$ peak of unspattered Cu/Ni/Si(100) along with the numerical deconvolution of peaks.

indicates the hole created in $2p$ level of Cu and $\underline{L}$ indicates a hole in ligand (oxygen) $2p$ level. The ground state of Cu^{2+} before photoemission from $2p$ level is known to be $3d^{10}\underline{L}$, where a hole is present in the ligand $2p$ level. The observed satellites correspond to the final state configuration, $2p_3d^9$ (Rosencwaig *et al* 1971; Kotani *et al* 1990). These satellites are called charge transfer satellites as the configuration occurs via charge transfer from metal $3d$ to ligand $2p$. Such satellites are observed only in Cu^{2+} compounds but not observed for pure Cu and Cu^{1+} compounds like Cu_2O as their ground state configurations do not contain holes in the ligand $2p$ level.

Figure 3 shows a two-dimensional 1000×1000 nm AFM image (upper panel) of as deposited Cu/Ni/Si(100). The lower panel of figure 3 shows sectional analysis along the straight line indicated in the AFM image. The sectional analysis shows that the average particle size on the surface of as

Figure 3. AFM topography and line profile of as deposited Cu/Ni/Si(100).

deposited sample is about 40 nm, indicating the formation of nano-structures on as deposited sample. Observed structures are mainly covered with adsorbed oxygen and carbon on the surface. Our XPS measurements indicated the formation of CuO on the surface. Such surface oxide formation is expected as the sample is exposed to ambient for AFM measurements after deposition. However, the adsorbed carbon is not chemically reactive to Cu.

Two-dimensional 100×1000 nm AFM images of Cu/Ni/Si(100) sputtered for 10 and 40 min are shown in Figure 4(a and b), respectively, and their sectional analyses along the straight lines drawn in the AFM images are shown in Figure 4(a' and b'). After 10 min sputtering, the surface exhibits a mound structure with an average particle size of about 100 nm as shown by the sectional analysis. These nanoparticles are of pure copper as confirmed by sharp and intense $2p$ peaks of Cu observed in our XPS measurements after 10 min sputtering. At this level the surface looks flat with no pits are mounds. After 40 min sputtering, the surface exhibits large pits of size ranging from 100 to 300 nm with an average depth of about 10 nm. These pits seem randomly positioned and contain some amount of Ni inside them as shown by weak Ni $2p$ signal in XPS measurements after 40 min sputtering.

4. Discussion

Ion bombardment on solid surfaces can induce physical and chemical changes. The low energy inert gas ions remove or

Figure 4. AFM topography (1000×1000 nm) of (a) 10 min and (b) 20 min sputtered Cu/Ni/Si(100) and their line profiles ((a') and (b')).

displace the surface atoms. When the ion is at a few Angstroms away from a solid surface, due to electron exchange processes, the ion captures electrons from the solid surface and gets neutralized. The recoil energy of energetic neutralized ion is dissipated in a series of collisions among neighbor atoms (Ziegler *et al* 1985). The localized recoil energy induces a thermal spike (Thompson 1981) resulting in the formation of disordered material (Caturla *et al* 1996; Nord *et al* 2002). Subsequent energy dissipation could result in isolated point defects (Marques *et al* 2007) and sputtering. Figure 5 shows the ion implantation profile of 3 keV argon ions bombarded normally on Cu surface calculated using Stopping and Range of Ions in Matter (SRIM) (Ziegler *et al* 1985) along with a numerical fit using the Gaussian function. The estimated ion projectile range of 2.47 nm suggests that the maximum damage takes place near the surface region. The nano-structures observed on as deposited Cu surface are covered with CuO as suggested by XPS studies. During the initial sputtering, oxygen has been preferentially sputtered from the surface of as deposited sample due to the high sputter yield of oxygen compared with Cu (Murti *et al* 1979; Medicherla *et al* 2010). The evolution of surface morphology is mainly caused by the erosion of surface atoms by ion beam (Cuerno and Barabasi 1995). The bombarding argon ions can transfer their kinetic energy to the atoms present on the surface region and below upto a few nm as shown in figure 5. The ion beam not only predominantly sputters atoms in the surface region but also creates defects below the surface region. Erosion of this sort is expected to remove

Figure 5. Ion implantation profile (dot) calculated using SRIM software and numerical fit (line) using a Gaussian function.

surface structures and produce a uniformly smooth morphology. We have observed somewhat smooth surface morphology (without pits) on the 10 min sputtered surface by erosion of oxygen. The energy transferred to the pure Cu layer below the oxide layer by the ions causes the particles to spear out in the plane as observed in AFM images (figure 3).

After the removal of oxide layer, the ion beam sputters the Cu layer. It produces ripples at off normal incidence and mounds or pits at normal incidence (Kahng *et al* 2001). Argon ion sputtering produced uniform holes or depressions on

copper surface (Rusponi *et al* 1998). Metallic single crystal surfaces like Cu(001), Ag(001) and Au(111) exhibit pits that reflect the symmetry of the crystal plane (Ritter *et al* 1996; Ernst 1997; Murty *et al* 1998). In our case, sputtering is done at near normal incidence and thus pits are expected rather than ripples. Our AFM morphology studies on the 40 min sputtered sample exhibited the formation of large pits of irregular shape and size. Nucleation of pits occurs at defects either created by the ion beam or originally present in the sample. These defects are expected to be distributed randomly on the surface and thus create randomly positioned pits. Variation in defect density could lead to the size distribution of the pits. Interestingly, the multiple interaction molecular beam dynamics simulations (Harrison and Webb 1983) indicated the formation of small pits on the Cu(100) surface by 5 keV argon ions. These pits are formed as a consequence of defects created by metal atom displacements. The weak nickel signal observed in XPS after 40 min sputtering is expected to arise only from the interior of the pits and the rest of the surface contains Cu. The Cu 2p_{3/2} peak shifting to higher binding energy after sputtering can be attributed to the surface damage caused by the ion beam. When bulk CuO is sputtered with 3 keV argon ion beam, it is reduced to a very stable Cu₂O (Panzner *et al* 1986). In our case, no Cu₂O formation is observed as our sample contains oxide only on the surface. The interfacial Cu 2p_{3/2} core level exhibits a large asymmetry compared to surface core level. The increase in asymmetry is because of increase in local density of states (LDOS) of Cu. In the interface region, the mixing of Cu and Ni leads to the formation of random CuNi alloys, increasing the LDOS of Cu.

5. Conclusions

Cu/Ni bilayer has been deposited on Si(100) surface by thermal evaporation of pure metals in high vacuum. As deposited Cu/Ni/Si(100) surface exhibits nano-structures of Cu covered with oxide. Sputtering the surface at low fluence gives rise to diffuse nano-structures of size 100 nm. High fluence sputtering leads to the formation of deep and wide pits of lateral size varying from 100 to 300 nm. The bottom surface of these pits contribute to the nickel signal observed in XPS.

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