Chapter 6

Electronic and Magnetic Properties of CuNi bilayer alloys

6.1 Introduction

Metallic multilayers are extensively used in industries and basic science due to their novel physical and engineering properties. Metallic multilayers exhibit improved electronic, magnetic and mechanical properties [142–144] compared to the pure metal constituents. They 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 due to 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 [145–147]. Cu/Ni layers are used in microactuators, nanomold for nanoprinting and magnetic devices [142,148–150]. Cu/Ni thin-film in a few micrometers thickness are often used as an integral part of multilayer metallizations on semiconductor chips and packages [151–154]. Magnetic multilayers are recently investigated due to their numerous applications in industries and also due to challenges they offer in basic science [155–157]. CuNi alloys have good durability in seawater and are used in desalination technology [158]. The corrosion resistance property of CuNi alloys makes them suitable for use as a protective coating in marine and corrosion environment [159].
The magnetic and mechanical properties of thin layers of Cu/Ni are different from those of homogeneous CuNi alloys or their metallic counter parts [75]. Theoretical investigations of Ni monolayer on Cu suggested a significant influence of the presence of Ni layer on the magnetic properties of the system [76]. The magnetic anisotropy in Cu/Ni/Cu(100) thin film system depends on the thickness of Ni layer and for thickness ranging from 15 to 135 angstrom, perpendicular magnetic anisotropy develops [77]. The magnetic moment in Ni/Cu/Si(100) system was found to decrease with the decreasing thickness [78]. There has been a great research in the development and characterization of Cu/Ni thin films due to their potential applications in erosion & corrosion resistance, operational amplifier, thin film resistor, microelectromechanical systems (MEMS) and sensor industry [160–165]. Systems of thin metallic multilayers have been used in magnetic recording and reading. Copper exhibits diamagnetic behavior [166] whereas Ni is ferromagnetic with a Curie temperature of 631K [167]. To overcome diamagnetic nature of Cu, above 0.8% Ni substitution is required [168]. The physical properties of the multilayer films depend on the thickness of each layer and also on the thickness and the quality of interface. Usually, interface exhibits physical properties that are drastically different from their metallic counter parts. Various studies have been conducted on interdiffusion in metallic multilayers, Cr/Cu, Au/Cu, Cu/Sn [169] and Au/Ni [170]. 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 [171, 172]. 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 [173, 174].

In this chapter, we report the Ar ion bombardment induced electronic, magnetic and morphological changes occurring in Cu/Ni bilayer deposited onto Si (100) by thermal evaporation method under high vacuum condition. The structural formation of Cu/Ni bilayer was studied by X-ray Diffraction (XRD) techniques, Core levels of the bilayer has been studied using X-ray Photoelectron Spectroscopy (XPS) technique, the surface morphology was investigated using Atomic Force Microscopy (AFM) technique and the magnetic properties were studied by using Superconducting Quantum Interference Device (SQUID) measurements.
6.2 Experiment

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 $2.0 \times 10^{-5}$ mbar. 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 few hours in vacuum chamber to remove the surface contamination. In the first step, a Ni layer of 40 nm thick is deposited on to the Si (100) substrate and subsequently a Cu layer of thickness 20 nm is deposited on top of the Ni layer. The structure of the films was studied using X-ray diffraction (XRD) technique and the surface morphology was studied by Atomic Force Microscopy (AFM) (Nanoscope III, Veeco) in tapping mode using SiN tip. The core levels of Cu/Ni thin film were studied using X-ray photoelectron spectroscopy (XPS). The magnetization in the sample was measured by SQUID-VSM.

Sputtering and XPS measurements were carried out in a VG ESCA machine (IOP, Bhubaneswar) equipped with an argon sputter gun, twin anode X-ray source and a hemispherical analyser. Sputtering was done using a 3 keV argon ion beam in-situ in the preparation chamber at a base vacuum of $2.0 \times 10^{-8}$ mbar. Argon ion current was fixed at 10µA using an argon pressure of $5.0 \times 10^{-6}$ 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 done in a de-focussed mode with a large spot size to cover whole of the sample. The uniformity of sputtering was assured by observing the XPS signals at different positions of the sample and found that the line profile of Cu 2p remains same. Sample has been sputtered for 10 min, 20 min and 40 min for which the ion fluences are given by $6.0 \times 10^{15}$, $1.2 \times 10^{16}$ ions/cm$^2$ and $2.4 \times 10^{16}$ ions/cm$^2$ respectively. The samples have been transferred to the analysis chamber having a base vacuum of $2.0 \times 10^{-10}$ mbar, immediately after sputtering, for XPS measurements. Samples have been exposed to ambient during the transport from thin film chamber to XPS chamber and again from XPS chamber to AFM measurements. Cu 2p and Ni 2p core level photoelectron peaks were measured at each sputtering time. The total energy 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 (B.E.) 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 SiN tip (dimension 5-10 nm) immediately after taking out the samples from XPS chamber.
6.3 Results

The XRD pattern of Cu/Ni/Si(100) film recorded using CuK$_\alpha$ radiation is shown in Fig. 6.1. The pattern shows the Bragg peaks corresponding to Cu, Ni and Si as indicated in the figure. The most intense (111) Bragg reflections of both Cu and Ni are merged and occur at around the same $2\theta$ angle of 43.46 degrees. The lattice parameter of Cu and Ni calculated using the Fullprof software for Cu/Ni film are 3.603 Å and 3.40 Å respectively which closely agree with the corresponding bulk values.

The crystallite sizes of these samples were calculated using the Scherrer equation, \[
t = \frac{0.89\lambda}{(\beta \cos \theta)}\]
where $\lambda$ is the wavelength of the X-ray source used, $\theta$ is the Bragg’s angle and $\beta$ is the full width at half maximum of the peak measured in radians [175]. The average crystallite size calculated using Scherrer equation is about 30 nm. The AFM topography of Cu/Ni/Si(100) surface is shown in the inset of figure 6.1. The picture clearly shows a uniform microstructure having maximum roughness of 5 nm. The average grain size is about 35 nm which is comparable to the crystallite size estimated from the XRD pattern in one plane.

Figure 6.1: XRD pattern of as deposited Cu/Ni/Si(100) and the inset shows the AFM topography
The magnetic field dependent magnetization at 300K and 5K temperatures is shown in Fig. 6.2. Interestingly, sample exhibits ferromagnetic behavior up to room temperature as shown by the hysteresis. Substrate Si and Cu are known to be diamagnetic in nature. Our sample contains 40 nm thick ferromagnetic layer sandwiched between two diamagnetic materials. Magnetization measured is an average magnetization of 20 nm thick Cu layer, 40 nm thick Ni layer and the Si substrate. In the copper layer magnetic moment is zero and increases gradually in the interface region and becomes maximum in the Ni layer. Therefore a week ferromagnetism is observed with very small magnetization in comparison to the magnetization of pure Ni. It is also reported that magnetic moment per Ni atom having hcp, fcc and bcc structures are within the range of 0.55-0.59 \( \mu_B \) \[176\] and for small clusters of Ni (8 to 200 atoms), the magnetic moment per Ni atom is greater than 0.8\( \mu_B \) \[177, 178\].

Our experimental value is estimated to be 0.38\( \mu_B \) per Ni atom which is lower than the theoretically predicted value. In compositionally modulated Cu/Ni films, an enhancement of magnetization was observed \[75\]. Our sample being only a bilayer, such enhancement was not observed. The field cooled (FC) magnetization continuously increases upto 40 K and then almost saturates for lower temperatures. However, the zero field cooled magnetization (ZFC) increases upto 40 K, attains a maximum value therein and then decreases. It is reported in literature \[179, 180\] that the coercivity of the magnetic samples is related to magnetic anisotropy and the shape of the FC and ZFC curve determine the role of anisotropy below the ordering temperature. Especially, magnetic anisotropy aligns the spins in a preferred direction. In ZFC magnetization measurements, no magnetic field is applied while cooling. Hence the spins are frozen in random direction for a polycrystalline specimen at low temperature and reduce the net magnetization. In field cooled magnetization measurements, a small field is applied at the lower temperature. Due to the low anisotropy, the spins flip their position according to the applied magnetic field and attain an ordering of spins. Hence the magnetic behavior observed in bilayer thin film is due to the low anisotropic feature of the Ni film \[181\].

Fig. 6.3 (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 Cu surface. It is clearly evident that the Cu 2p_{3/2} peak splits into two. Such splitting is not apparent in Cu 2p_{1/2} peak due to low intensity and the increased energy width of the 2p_{1/2} peak compared to that of 2p_{3/2} peak is due to Coster-Cronig transitions. After sputtering,
Figure 6.2: Magnetic hysteresis of Cu/Ni/Si(100) and the inset shows the temperature dependence of magnetization

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 was carried out only in $2.0 \times 10^{-5}$ mbar pressure. In this case deposition was done 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. Ni 2p core level is observed only after sputtering the sample for 40 min and is shown Fig. 6.3(b). Ni $2p_{3/2}$ occurs at a binding energy of 853.0 eV with a spin orbit splitting of 17.5 eV.

Fig. 6.4(a) shows the Cu $2p_{3/2}$ peak of Cu/Ni/Si(100) after sputtering for 10 min, 20 min and 40 min along with the 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, Cu $2p_{3/2}$ peak shifts to higher binding energy by 0.1 eV. The LW and asymmetry parameter were found to be same as those of 10 min sputtered sample. Interestingly, 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 after 40 min sputtering. Fig. 6.4(b) shows Cu $2p_{3/2}$ peak of unsputtered sample. This spectrum has been decomposed into
Figure 6.3: (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.

Four peaks as shown in the figure. The two main peaks at 932.4 eV and 934.7 eV correspond to pure Cu metal and CuO respectively. The low intense features at 940.7 eV 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 to the value reported for bulk CuO [182]. 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 $2p3d^{10}L$ configuration where $2p$ indicates the hole created in 2p level of Cu and $L$ indicates a hole in ligand (oxygen) 2p level. The ground state of Cu$^{2+}$ before photoemission from 2p level is known to be $3d^{10}L$ where a hole is present in ligand 2p level. The observed satellites correspond to the final state configuration, $2p3d^9$ [182, 183]. 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$^{+}$ compounds like Cu$_2$O as their ground state configurations do not contain holes in ligand 2p level.
Figure 6.4: (a) Cu 2p$_{3/2}$ spectra of Cu/Ni/Si(100) sputtered for (1) 10 min (2)20 min and (3) 40 min. Dots represents 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 unsputtered Cu/Ni/Si(100)along with the numerical deconvolution of peaks

In Fig. 6.5, the Cu 2p$_{3/2}$ core level of 10 min sputtered (pure Cu surface) and 40 min sputtered (Cu/Ni interface region) along with the Doniach - Sunjic (DS) line shape fitting are shown. In the original data interfacial core level exhibits a shift of 0.3 eV towards high binding energy compared to surface core level. They have been aligned to the same energy, i.e. 932.4 eV as our interest is to emphasize the changes occurring in line shape. Interestingly, the interface core level is highly asymmetric with an asymmetry parameter of 0.11 compared to low asymmetric surface core level with asymmetry parameter 0.07.

Fig. 6.6 shows the two-dimensional 1000 nm×1000 nm AFM image (upper panel) of as deposited Cu/Ni/Si(100). The lower panel of Fig.6.6 shows the sectional analysis along the straight line indicated in the AFM image. The sectional analysis shows that the average particle size on the surface
The two-dimensional 1000 nm × 1000 nm AFM images of Cu/Ni/Si(100) sputtered 10 min and 40 min are shown in Fig. 6.7(a) and Fig. 6.7(b) respectively and their sectional analysis along the straight lines drawn in the AFM images are shown in lower panels of Fig. 6.7(a′) and Fig. 6.7(b′). After 10 min sputtering, surface exhibits a mound structure with an average particle size of about 100 nm as shown by the sectional analysis. These nano particles 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 surface looks flat with no pits are mounds. After 40 min sputtering, surface exhibits large pits of size ranging from 100 to 300 nm with an average depth of about 10 nm. These pits seem to have randomly positioned and contain some amount of Ni inside them as shown by weak Ni 2p signal in
6.4 Discussion

Ion bombardment on solid surfaces can induce physical and chemical changes. The low energy inert gas ions remove or displace the surface atoms. When the ion is at 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 [184]. The localized recoil energy induces the thermal spike [185] resulting in the formation of disordered material [186, 187]. Subsequent energy dissipation could result in isolated point defects [188] and sputtering. Figure 6.8 shows the ion implantation profile of 3 keV argon ions bombarded at the direction of the surface normal of the Cu surface calculated using Stopping and Range of Ions in Matter (SRIM) [184] along with a numerical fit using the Gaussian
Figure 6.7: AFM topography (1000 nm × 1000 nm) of (a) 10 min (b) 20 min sputtered Cu/Ni/Si(100) and their line profiles ((a′) and (b′)).

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 to Cu [171, 189]. The evolution of surface morphology is mainly caused by the erosion of surface atoms by ion beam [190]. The bombarding argon ions can transfer their kinetic energy to the atoms present on the surface region and below up to few nm as shown in Fig. 6.8. 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 surface structures and produce a uniformly smooth morphology. We have observed some what smooth surface morphology (without pits) on 10 min. sputtered surface by the erosion of oxygen. The energy transferred to the pure Cu layer below the oxide layer by the ions have caused the particles to spread out in plane as observed in AFM images (Fig. 6.7).
After the removal of oxide layer, ion beam sputters the Cu layer. Ion beam produces ripples at off normal incidence and mounds or pits at normal incidence [191]. Argon ion sputtering produced uniform holes or depressions on copper surface [192]. Metallic single crystal surfaces like Cu(001), Ag(001) and Au(111) exhibit pits that reflect the symmetry of the crystal plane [193–195]. In our case sputtering is done at near normal incidence and thus pits are expected rather than ripples. Our AFM morphology studies on 40 min sputtered sample exhibited the formation of large pits of irregular shape and size. Nucleation of pits occur 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 creating randomly positioned pits. Variation in defect density could lead to the size distribution of the pits. Interestingly, the multiple interaction molecular beam dynamics simulations [196] 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. 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\textsubscript{3/2} peak shift 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 Cu\textsubscript{2}O [197]. In our case, no Cu\textsubscript{2}O formation was observed as our sample
contains oxide only on the surface. Asymmetry in XPS core levels is directly related to the occupied local density of states (LDOS) of the corresponding atomic site (Cu). The large increase in asymmetry of the interface core level indicates strong Cu-Ni interactions in the interface region. Due to these interactions charge transfer from Ni to Cu takes place and increase of LDOS of Cu occurs [198]. We believe that Cu-Ni interactions in the interface region lead to magnetic anisotropic feature at 40K as observed in magnetization data.

6.5 Conclusion

Cu/Ni bilayer has been prepared by thermal evaporation of pure Cu and Ni metals onto Si(100) surface in high vacuum and was sputtered using argon ion beam in ultra high vacuum. The ion beam induced surface interface modification and magnetic properties were investigated using X-ray diffraction, Atomic Force Microscopy, Superconducting Quantum Interference Device (SQUID) measurements and X-ray Photoelectron Spectroscopy. As 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 $6.0 \times 10^{15} \text{ions/cm}^2$, surface exhibits a mound structure with an average size about 100 nm. Interestingly, sputtering at higher fluence of $2.4 \times 10^{16} \text{ions/cm}^2$, surface exhibits broad pits of sizes ranging from 100 to 300 nm with an average depth of 10 nm. Bottom surface of these pits contain Ni atoms. 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 to pure copper. These changes are attributed to Cu-Ni interactions at the interface. Observed ferromagnetic behavior of Cu/Ni film is attributed to Ni-Ni interaction as Si and Cu are diamagnetic in nature. The variation in field cooled and zero field cooled magnetic measurements indicate the presence magnetic anisotropy. Cu-Ni interactions at the interface lead to the observed magnetic anisotropy.