Chapter 7

Summary and Conclusions
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In this thesis, three material systems, Cu$_{1-x}$Ni$_x$ and Ag$_{1-x}$Pd$_x$ bulk disordered alloys and also Cu/Ni bilayer on Si(100) surface have been investigated using Photoelectron Spectroscopy (PES), Atomic Force Microscopy (AFM) techniques and SQUID Magnetometer. All the samples have been characterized structurally using x-ray diffraction (XRD) technique.

Bulk alloys have been prepared by arc melting method and were annealed in high vacuum for better homogeneity and grain sized lattice parameter of both Cu$_{1-x}$Ni$_x$ ($x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0$) and Ag$_{1-x}$Pd$_x$ ($x = 0, 0.02, 0.05, 0.1, 0.15, 0.25, 1.0$) alloys exhibit a linear dependence with composition suggesting the formation of disordered alloys. Electronic structure of these alloys has been investigated using high resolution Photoelectron Spectrometer equipped with monochromatic AlK$_\alpha$ and He I radiation sources and a Scienta R4000 analyser. Experiments were carried out in an ultra-high vacuum of $10^{-11}$ Torr. The bulk alloys have been scrapped with a diamond file prior to the data acquisition in the above vacuum to obtain a fresh surface without contamination. The resolution of the spectrometer as determined prior to the experiments were found to be 0.39 eV (varies between 0.35 - 0.39 eV depending on the settings) with monochromatic AlK$_\alpha$ radiation and 3.5 meV with He I radiation. Cu 2p, Ni 2p, Ag 3d, Pd 3d core levels and valence bands, Cu L$_3$M$_{4,5}$M$_{4,5}$, Ni L$_3$M$_{4,5}$M$_{4,5}$ and Ag M$_{4,5}$ VV, Pd M$_{4,5}$ VV Auger spectra have been obtained using monochromatic AlK$_\alpha$ radiation for bulk alloys. High resolution valence band of Cu$_{1-x}$Ni$_x$ alloys with monochromatic He I radiation was recorded to elucidate the formation and evolution of virtual bound state of Ni 3d states. Resolution in the XPS valence bands was not sufficient for the purpose in case of CuNi alloys, where as in AgPd alloys, observation of virtual bound state was possible with XPS.

Cu/Ni bilayer has been deposited on silicon surface in high vacuum of 2 x $10^{-5}$ mbar by thermal evaporation of Cu and Ni. Prior to the deposition, Cu and Ni metals along with Si wafer have been degassed in the vacuum system to get rid of the contamination. Cu/Ni bilayer on Si(100) has been investigated using un-monochromatized AlK$_\alpha$ X-rays with a total resolution of 0.9 eV in VG ESCA system under a vacuum of 2 x $10^{-10}$ mbar. In-situ argon ion sputtering is used to study the ion beam effects on Cu/Ni bilayer. Sputtering was done using a 3 keV argon ion beam maintaining an argon partial pressure 5 x $10^{-8}$ mbar at fluences 6.0 x $10^{15}$, 1.2 x $10^{16}$ and 2.4 x $10^{16}$ ions/cm$^2$. XPS and
AFM studies have been done on as deposited and sputtered samples. AFM measurements were done ex-situ immediately after completing XPS measurements.

CLSs of both Cu and Ni core levels are negative in Cu$_{1-x}$Ni$_x$ alloys. Both the core levels shifts to lower binding energy with respect to their metal counterpart giving rise to negative CLS. This implies that the major contribution to CLS in this alloys series is primarily due to the shift in Fermi energy. In a free electron like system, the position of the Fermi level depends on the number density of free electrons. When Ni is substitute into Cu the electron density decreases by 1 for each Ni atom causing the Fermi level to shift down, which in turn cause the decrease in binding energy of the core electrons in the alloys compared to the pure metal counterparts. Therefore the CLS becomes negative as it is defined as the binding energy of the core level in the metal subtracted from that of in alloys. Cu 2p core level exhibits disorder broadening (CDB) with highest value being 0.35 eV for 90% Ni alloy. It is expected that the CDB be maximum at 50%. This anomalous was explained by charge excess functional model which takes care of segregation effects. Surprisingly, Ni 2p becomes narrower as the Cu content increases in the alloy. One usually would expect Ni 2p also to broaden with the increase of Cu content in the alloy taking disorder into consideration. There are two contribution to the line width namely natural broadening (Lorentzian type) and disorder broadening (Gaussian type). Natural broadening is atomic in nature and is not expected to vary from pure metals to alloys. All the model and theoretical calculations are done assuming same natural broadening in the metal and corresponding alloys. This assumption seems to be failing in CuNi alloys where strong MM Auger transitions which may increase the core hole life time and indirectly decrease the natural broadening in alloys compared to pure Ni.

The valence band spectra of Ag$_{1-x}$Pd$_x$ ($x = 0, 0.02, 0.05, 0.1, 0.15, 0.25, 1.0$) disordered alloys exhibit the formation of Pd 4$d$ virtual bound state on that sp states of Ag. The virtual bound state broadens up with the increase of Pd content. CLS of Ag 3$d$ is negative and the magnitude increases linearly with Pd concentration in the alloy. Interestingly Pd 3$d$ core level exhibits positive CLS for the compositions studied in this thesis which do not follow a linear behavior with Pd concentration. Core Disorder Broadening (CDB) of Ag 3$d$ was insignificant up to the alloys corresponding to $x = 0.1$ alloy. But, a significant CDB has been observed for $x = 0.15$ and $x = 0.25$ alloys. Pd 3$d$ core level of pure Pd is highly asymmetric and broad. Pd 3$d$ spectra of alloys are very sharp and could be described as a single DS profile. CDB was not observed in Pd 3$d$ core level. The width of Pd 3$d$ core level of alloy with low Ag content (75%) is broader than that of the alloy with high silver content (95%) indicating the manipulation of Pd 3$d$ core hole life time upon alloying with Ag.
X-ray excited Auger Electron Spectroscopy has been used to investigate the Auger transition Cu(Ni)L₃M₄.₅M₄.₅ and Ag(Pd) M₄.₅VV in Cu₁₋ₓNiₓ and Ag₁₋ₓPdₓ disordered alloys. Cu L₃M₄.₅M₄.₅ Auger peak exhibits composition dependent Auger shift and disorder broadening, whereas the Ni L₃M₄.₅M₄.₅ exhibits drastic changes of shape which makes the estimation of shift and broadening unrealistic. Ag M₄.₅N₄.₅N₄.₅ Auger profile also exhibits composition dependent kinetic energy shifts and disorder broadening. The kinetic energy shift of Ag M₄.₅N₄.₅N₄.₅ varies as \(c^{1/2}\), where \(c\) is the Pd concentration in the alloy. On the other hand, Pd M₄.₅N₄.₅N₄.₅ Auger profile exhibits dramatic changes of relative intensities of the fine features with composition. It is difficult to find the kinetic energy shifts and broadening effects in Pd M₄.₅N₄.₅N₄.₅ Auger spectra due to dramatic changes occurring in the line profile with composition. Ag M₄.₅N₄.₅N₄.₅ Auger transition exhibits atomic nature due to localized nature of Ag 4d states and Pd Auger exhibits quasi atomic behaviour due to the partly delocalized nature of Pd 4d states.

As deposited Cu/Ni bilayer on Si(100) surface 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 \(2.4 \times 10^{16} \text{ions/cm}^2\), causes the formation of 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. Interfacial Cu 2p₃/₂ 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 which 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 of magnetic anisotropy.
Scope of the Future Work

Ni and Pd being transition metals which are one of the constituents of the disordered alloys Cu_{1-x}Ni_x and Ag_{1-x}Pd_x, studies in this thesis contain partially filled d bands and form virtual bound states for low concentrations. When transition metals are alloyed with noble metals, the core level photoelectron peaks of the transition metal is expected to broaden up as noble metal introduces disorder into the transition metal. This was not observed, but surprisingly, alloy core level of the transition metal is sharper than the pure metal core level and the sharpness increases with the increase of noble metal concentration. It looks like core hole life time is increasing with the increase of noble metal content in the alloy. This will give rise to a drastic decrease of Lorentzian broadening. At present all models assume core life time remains same in pure metals and alloys. A more versatile model which can include the core hole life time as a variable parameter can explain the behavior of sharpening of the transition metal core levels. It can be further verified experimentally by alloying two transition metals (Ni and Pd) together and look at the widths of the core levels of both. Similarly, one can also verify by alloying two noble metals (Cu and Ag) if they are immiscible. These studies could provide some insight into the anomalies observed in the core levels of Ni and Pd.