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Synthesis of Cu/Ni thin film by thermal evaporation technique and its XPS study

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Abstract : In this article, the synthesis of Cu/Ni bilayer thin film and surface sensitivity of XPS technique has been discussed. To understand surface sensitivity of XPS technique, Cu/Ni thin films were prepared by thermal evaporation technique. Nickel metal of purity 99.99 % is deposited on silicon (100) substrate by thermal evaporation method. Then copper metal of purity 99.99 % is deposited on top of the Ni layer. The thickness of the nickel is about 40 nm on the silicon and the thickness of Cu on Ni is about 30 nm. It is experimentally observed that in such a situation the XPS signals due to the substrate (both Ni and Si) are rapidly attenuated, while those due to the condensed evaporator (Cu metal) simultaneously increase to limiting value. The intense peaks of Cu compare to Ni confirm that XPS technique is very surface sensitive.

Keywords: X-ray photoelectron spectroscopy (XPS), parts per million (ppm), Spin-Orbit-Splitting (SOS)

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1. Introduction

The basic principle of X-ray photoelectron spectroscopy (XPS) is based on photoelectric effect. Einstein has explained photoelectric effect with the help of the photon picture of radiation in 1905 [1]. The technique is used to emit electrons from solids with incident of suitable photon energy. In fact, it has a long history that can be traced to contemporary measurements in which either X-rays or gamma rays were used to excite photoelectrons from solids [2]. The experimental success of photoelectric effect in late 1950s, gives a hope for the development of new technique called as X-ray Photoelectron Spectroscopy (XPS) [3-13] to study composition and electronic structure of matter. XPS is high sophisticated technique used to analyze metal alloys [14-19], thin films, semiconductors, bio-science, catalysts, ion modified materials and many others.

There has been a tremendous progress 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 [20-25]. 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. Due to potential applications of XPS in different branches of science and engineering, it encourages to discuss the surface sensitivity of this technique.

However, the importance of structural and core level studies of Cu and Ni has not been done at interface region or interior region from the surface. The XPS study on lower surface has already been published elsewhere. Hence in this paper, the core level spectrum studies has been done only on the surface to see that whether any structural change has been obtained due to deposition of Cu over Ni surface as growth thickness is higher than the penetration depth of X-ray in XPS.

2. Experimental Technique

X-ray photoelectron Spectroscopy is a surface sensitive spectroscopy technique that allows chemical identification of the elements in the top atomic layers of a sample by recording the binding energies of the electrons associated with these atoms. The sensitivity boils down to whether it is possible to detect the desired signal above the noise level. To demonstrate the XPS surface sensitivity, Cu/Ni thin films were deposited by thermal evaporation of pure copper (99.99%) and pure nickel (99.99%) metals onto a Si (100) substrate kept at room temperature. 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 30 nm is deposited on top of the Ni layer. The surface core levels of Cu/Ni thin film were studied using X-ray photoelectron spectroscopy (XPS). XPS measurements were carried out in a VG ESCA system using AlKα (1486.6 eV) radiation with a total resolution of 0.9 eV measured as the reference of carbon binding energy at 284.6 eV.

3. Result and Discussion

The XPS technique is highly surface specific due to the short range of the photoelectrons that are excited from the solid. The binding energy of the peaks is characteristic of each element. The peak areas can be used (with appropriate sensitivity factors) to determine the composition of the materials surface. But a major problem that needs to be addressed in surface spectroscopy is distinction between signals from the surface and the bulk of the sample. In principle, there are two ways that signals are recorded (1) surface signal is distinguishable from the comparable bulk signal (2) the vast majority of detected signal comes from the surface region of the sample. The second approach which is used by the majority of surface spectroscopic techniques is said to be surface sensitive.

To explain surface sensitivity of XPS technique, Cu/Ni thin films were prepared by thermal evaporation technique. It is possible to measure deposition rates using equipment such as quartz crystal oscillators and thus obtain independent verification of the deposited film thickness [26]. A detailed analysis of the variation of the signals due to Cu and Ni is also capable of yielding information about the mechanism of film growth. The XPS peak signal of carbon = 284.6 eV is taken as reference to calibrate the intensity of the Cu present on the top of the film as shown in Figure 1. Survey scan of the XPS signal of silicon reveals that there is no signal of present of silicon. (shown in Figure.2). Similarly, the present of nickel is not found from the survey scan of the film shown in Figure.3. The presence of Cu on the top of the film is confirmed from the XPS signal of Cu $2p_{1/2}$ at 953 eV and Cu $2p_{3/2}$ at 933.22 eV in survey scan as shown in Figure 4. Binding energy difference of Cu $2p_{1/2}$ and Cu $2p_{3/2}$ peaks due to the Spin-Orbit-Splitting (SOS) contribution is 19.78 eV, which is well matched with existing literature [27-28] and confirm the formation fo Cu/Ni thin film.

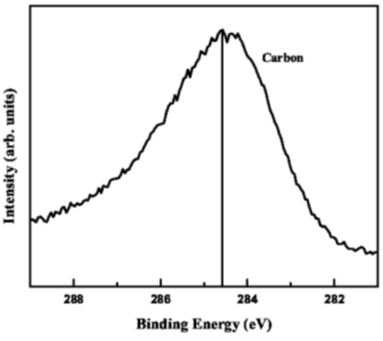


Fig. 1. XPS peak of carbon as reference at 284.6 eV

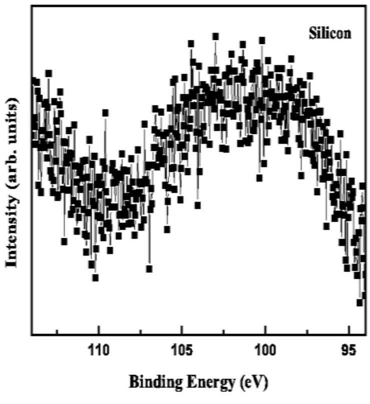


Fig. 2. Survey scan XPS signal of silicon (100) substrate

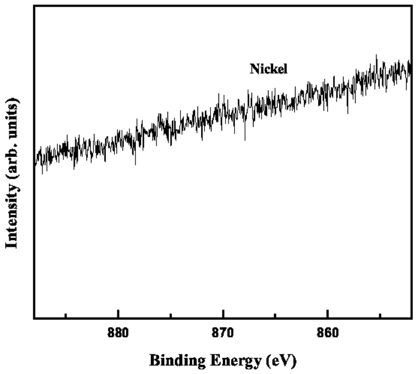


Fig. 3. XPS signal of Nickel element in Cu/Ni thin film

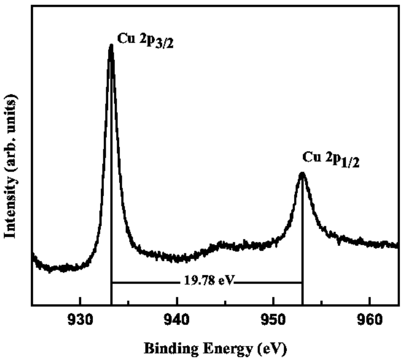


Fig. 4. XPS signal of Copper element in Cu/Ni thin film

In XPS, the used X-rays can penetrate a small distance into the sample (~µm). The surface sensitivity must therefore arise from the emission and detection of the photoemitted electrons from the sample surface. Consider a Cu/Ni thin film in which electrons of Cu atoms of given energy E_0, are emitted from Cu/Ni thin film at various depths, *d*, below a flat top surface as shown in Figure 5.

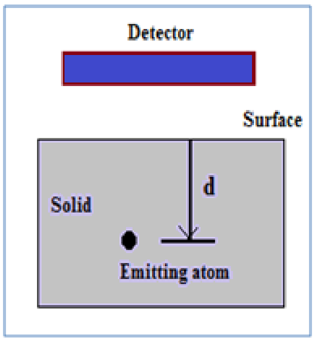


Fig. 5. Emission of electrons from Cu atoms from certain depth of the Cu/Ni thin film

Now it is assumed that only those electrons which reach the surface still have their initial energy (E_o). But in XPS experiments it is only those photoelectrons possessing characteristic emission energies and contributing to the peaks are considered. There are two possible ways in which the characteristic of the detected electrons can be analysed (i) some of them were captured before reaching the surface, or emitted in the wrong direction and never reached the surface (ii) some of other lost energy before reaching the surface.

The process loss of energy by photoelectrons during the journey through the solid is known as inelastic scattering. Each inelastic scattering event results (i) a reduction in the electron energy (ii) a change in the direction of travel. Several methods have been suggested to subtract this inelastic background from the initial spectrum. Among these, Shirley [29], Tougaard [30] and straight line [26] methods are in practice the most commonly used procedures. Figure 6 shows different possible trajectories of emitted electrons from a Cu atom. Clearly if the Cu atom had been closer to the surface, then a greater fraction of the emitted electrons would have been detected because of (i) the detector would subtend a greater (solid) angle at the emitting Cu atom (ii) for an electron emitted towards the surface, there would be less chance of inelastic scattering before it escaped from the film. *P(d)* is the probability of escape those electrons of Cu atoms which not being inelastically scattered during its journey to the surface. So it is clearly, $P(d_2) < P(d_1)$ explaining there will be always less probability for electron to reach surface from deeper portion of the solid. (shown in Figure.7). Inelastic Mean Free Path (IMFP) is a measure of the average distance travelled by an electron through a solid Cu metal before it is inelastically scattered. Normally, it depends upon (i) the initial kinetic energy of the electron and (ii) the nature of the solid. Without inelastic scattering, the IMFP in the function of depth d can be written as $P(d) = e^{\left(-\frac{d}{\lambda}\right)}$, where λ is the IMFP for the electrons of energy E.

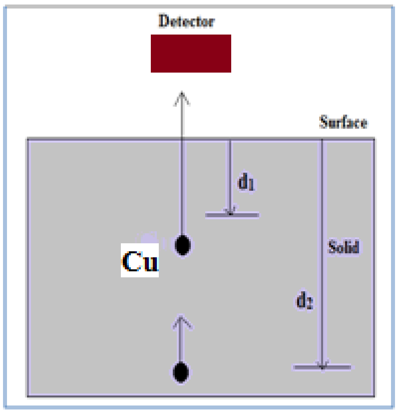


Fig. 6. Emission of electrons from Cu atoms from different depths of the Cu/Ni thin film.

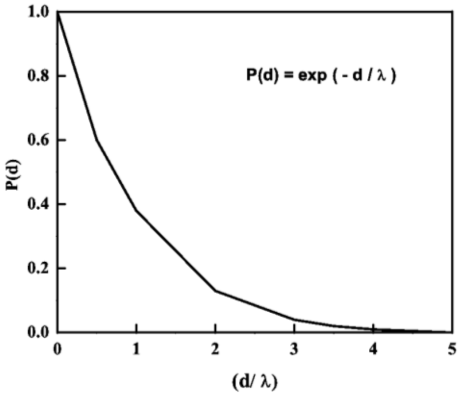
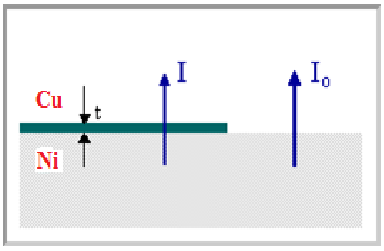


Fig. 7. Probability of emission of electrons from Cu atoms from top of the Cu/Ni thin film

In summary, The Inelastic Mean Free Path (IMFP) in metals is typically less than 10 Å for electron energies in the range 15 eV< E < 350 eV, 20 Å for electron energies in the range 10 eV < E < 1400 eV i.e. the IMFP of low energy electrons corresponds to only a few atomic layers. This means that any experimental technique such as XPS which involves the generation and detection of electrons of such energies will be surface sensitive.

To calculate the thickness of the Cu/Ni thin films by XPS measurements, consider a situation where a substrate Ni, is covered by a thin film of a Cu. The

XPS signal from the underlying Ni will be attenuated due to inelastic scattering of some of the photoelectrons as they traverse through the layer of Cu metal. The probability of such a scattering event for any single photoelectron passing through this layer is simply given by $P(t) = e^{\left(-\frac{t}{\lambda}\right)}$, where: *t* is the thickness of the layer of material Cu. It follows that the overall intensity of a XPS signal arising from Ni is reduced by this same factor, i.e. if the intensity of this signal in the absence of any covering layer is I_o, then the intensity *I* in the presence of the over layer is given by $I = I_0 e^{\left(-\frac{t}{\lambda}\right)}$ The thickness of the film can be calculated if spectra are acquired before and after deposition of the covering film.



4. Conclusion

In this article, attempt has been made to explain synthesis of Cu/Ni thin films and surface sensitivity of XPS technique. The XPS study of Cu/Ni thin films reveals that the signals strength of Si and Ni were very weak, all most zero where are intense XPS peaks of Cu metal are present. The intense XPS peaks of Cu on the top of the Cu/Ni films are predominate and SOS energy difference between Cu $2p_{1/2}$ and Cu $2p_{3/2}$ peaks is 18.78 eV confirm the presence of Cu on the top of the films. The above confirmation proves that synthesis of Cu/Ni thin films on the substrate Si (100) and surface sensitivity of XPS technique.

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