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X-ray photoelectron study of annealed Co thin film on Si surface

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ABSTRACT

The X-ray photoelectron spectroscopy (XPS) study on as deposited as well as 500 °C annealed Co (400 Å)/Si thin film synthesized by electron beam evaporation technique under UHV conditions is reported here. The XPS measurements carried out on as deposited sample rule out the possibility of any phase formation at room temperature. Whereas in 500 °C annealed sample the Co-$2p_{3/2}$ peak is observed at ~778.6 eV binding energy position, where the peak expected due to $CoSi_2$ resides. The Auger parameters were also calculated at each step of experiment because Auger parameter is always very sensitive to changes in the chemical state of the material. The recorded spectrum on annealed sample shows Auger parameter value of ~1551.4 eV, which is different from that observed in the as deposited sample (~1552.1 eV). The obtained results are analyzed and interpreted in terms of $CoSi_2$ phase formation at the interface with annealing.

1. Introduction

In recent years, the experimental and theoretical investigations of metal overlayer on semiconductor surface have witnessed a rapid growth. Due to the technological importance of transition metal silicide in integrated circuit technology and scientific interest about the effect of adlayer on Si substrate reconstruction and heterodiffusion, the properties of metal on Si surface have been widely studied [1–3]. In this respect, the interface between Co and Si has been the focus of the research due to its lower resistivity, small lattice mismatch with silicon, sharp interface (ideal for making schottky barrier) and high temperature stability. Cobalt silicide is used mainly in electronic devices as a contact material [4–6]. However, the interaction of Co with Si is not fully understood and controversies exist about the nature of Co/Si system. Various questions such as the prediction of the phase which will precipitate among the different phases exist for Co/Si system, how thick will be the silicide layer formed at the interface, and the details about electronic properties of Co/Si interface and how these properties are influenced by annealing remain unresolved.

It is well known that deposition of Co on Si and subsequent annealing it at different temperatures produces different phases of Cobalt silicide. The kinetics of formation of reaction between Co and Si was investigated by many researchers and various models were proposed to reveal the basic physics behind it [7–9]. The basic mechanism involves mainly three parameters: diffusion, thermodynamics barrier and reaction between them. The mass transport in Cobalt silicides can be classified into two categories i.e. grain boundary diffusion and volume diffusion. The activation energy for diffusion is linked to the enthalpy of formation and migration of these defects. In Cobalt silicides, the grain boundary diffusion coefficient dominates because its magnitude is five to six orders higher than the volume diffusion coefficient [10]. Also, the nucleation barrier which needs to be overcome to form a phase mainly depends on the free energy of formation and the surface energy term ($\Delta\sigma$). This energy also depends on the lattice match between different phases and on the temperature. Consequently, formation of different silicides depends on the lattice match with crystalline Si substrate and the interface structure. The third term (reaction) is responsible for the formation of one phase among the various phases available for silicides. At microscopic level, it depends on the thermodynamics and the mobility of reactants decides which phase will form initially [11–13]. The phase formation in Co and Si is reported by various authors and reported that annealing of Co on Si produces Co_2Si phase (~300 °C) at first. After that if the Co_2Si reaches a critical thickness then CoSi is formed. Finally $CoSi_2$ phase (~500 °C) is formed. However, many other authors have reported that CoSi is the first phase formed among the several phases of Cobalt silicides. [14,15]. However, Co_2Si as a first phase of Cobalt silcides is also reported in the literature [16]. Contrary, to these spontaneous formations of $CoSi_2$ at room temperature is also observed [17]. The disagreement among these results may be due to different deposition and other experimental conditions. It is also believed that stress [18], annealing temperatures [19], annealing environment [20], capping

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layer [21] and deposition parameters [22] strongly influence the formation of Cobalt silicide.

It has also been reported that among various phases of Cobalt silicides, $CoSi_2$ with a lattice parameter (5.365 Å) very close to that of a Si (5.341 Å) allows the growth of films with almost perfect interfaces, a feature essential for determining the electronic properties of the devices. Epitaxial nature of $CoSi_2$ is an important parameter in microelectronic industry [23,24]. One can expect the geometrical similarity between $CoSi_2$ and Si (1 0 0) substrate favors easy epitaxial growth of $CoSi_2$ on Si (1 0 0) [25–28]. However, the expected (2 0 0) and (4 0 0) reflections which are the characteristics of epitaxial alignment is absent in such case. The introduction of intermediate layer such as Ti, Ta and Zr, C between Co and Si enhances epitaxial growth of $CoSi_2$ on Si (1 0 0). It was reported that these refractory metal reduce native oxide layer that resulted smooth interface between $CoSi_2$ and Si [29–32]. However, $CoSi_2$ layer can also grow epitaxially on Si (1 1 1) substrate without the introduction of any intermediate layer, because in this case $CoSi_2$ (1 1 1) plane matches with Si (1 1 1) orientation plane [33].

To obtain detailed knowledge of the system, the authors have investigate interface electronic and chemical properties of Co/Si structure using X-ray photoelectron spectroscopy (XPS) technique on as deposited as well as 500 °C annealed film. The short inelastic mean free path of photoelectrons makes XPS a surface sensitive technique, giving information only up to few Angstrom of thickness further making it easy to probe the surface/interface electronic properties. The Auger parameter was also calculated from the Auger features to support the photoemission results.

2. Experimental details

Before deposition, ex-situ cleaning of the substrates was done using the following chemical method: the *n*-type Si (1 0 0) wafer used in present study was initially washed several times with soap solution and rinsed with distilled water. After that it was kept in the chemical solution of $HF:H_2O$ (volume ratio 1:50) for 1 min followed by rinsing with de-ionized water for removing organic contamination and finally cleaning with ultrasonic waves and drying using infrared lamp.

400 Å thicknesses of Co thin films were deposited using electron beam evaporation system on these substrates under UHV conditions. The deposition was carried out at a base pressure of $\sim 1 \times 10^{-9}$ Torr with 0.1 Å/s deposition rate. The annealing treatments were carried out at 500 °C for an hour under high vacuum environment.

All the XPS investigations on as deposited and 500 °C annealed Co/ Si films were carried out on OMICRON EA-125 Photoelectron spectrometer at a base pressure of better than $\sim 1 \times 10^{-10}$ Torr. Al-Kα un-monochromatized X-rays (1486.6 eV), with the source operated at an emission current of 10 mA and an anode voltage of 10 kV were employed for the analysis. The samples were properly grounded in order to avoid any charging effect. The hemispherical energy analyzer was used in the fixed analyzer transmission mode with adjustments in the pass energy to give an overall resolution of approximately 0.8 eV. Au-$4f_{7/2}$ at 84.0 ± 0.1 eV binding energy (B.E.) served as an external reference. For all the XPS measurements pass energy was kept constant at 50 eV. To correct the shifts in B.E of core levels due to charging effect, graphitic C-1s at 284.7 eV has been used as an internal reference. The depth profiling of the sample was done using low energy de-focused Ar^+ ion gun (to avoid ion beam mixing) attached to the spectrometer at oblique incidence, with the Ar^+ ion energy and ion beam current kept at ~1 keV and ~1 μA respectively.

Quantitative analysis of the composition of the films was performed by collecting the integrated intensities of C-1s, O-1s and Co signals using the Wagner's sensitivity factors [34]. The XPS peak areas and peak decompositions (i.e. curve fitting) were determined using XPSPEAK 4.1 software [35]. This software provides a fitting based on Newton's iterative method and allows one to subtract one of the three most commonly considered background types namely Shirley, linear or Tougaard [36]. Prior to fitting, Shirley background was subtracted and then peaks were de-convoluted according to their spin-orbit splitting. The B.E. positions thus obtained were used in the interpretation of these spectra. All these measurements were carried out in a vacuum better than $\sim 5 \times 10^{-10}$ Torr and at room temperature.

3. Results and discussion

In order to investigate the species present on top of the surface, XPS survey scans were recorded on as deposited sample as a function of sputtering time as depicted in Fig. 1. It can be clearly seen that the as deposited sample mainly contains photoemission peaks due to oxygen and carbon, at B.E. positions ~531.6 eV and ~284.6 eV respectively due to atmospheric exposure during sample transfer in XPS chamber. In addition to this, the small peaks due to Co-2p are also seen in the spectrum. The minor presence of these Co photoelectron peaks is expected due to presence of O and C on top of the surface, which suppresses the Co photoemission intensity.

The presence of O on top of surface was also reflected in XRR pattern, which showed ~11 Å oxide layer on top of Co surface [37]. In order to gain more insight of the system the sample was sputtered for different sputtering times, which shows systematic removal of O and C from the deposited sample. The spectrum recorded after 40 min sputtering shows elemental Co with different peaks such as Co-2p, Co-3s and Co-1s at their respective B.E. positions. In order to investigate the interaction of Co with Si at interface, the film was further sputtered to reach the interface region. With sputtering Si peaks start appearing with reduction in Co peak intensities showing the evolution of buried interface. The spectrum recorded after 50 min sputtering shows peaks due to both Co and Si, which indicate the signals are now coming from the interface region of Co and Si. The exact B.E positions of core level in each case were recorded in separate detailed scans.

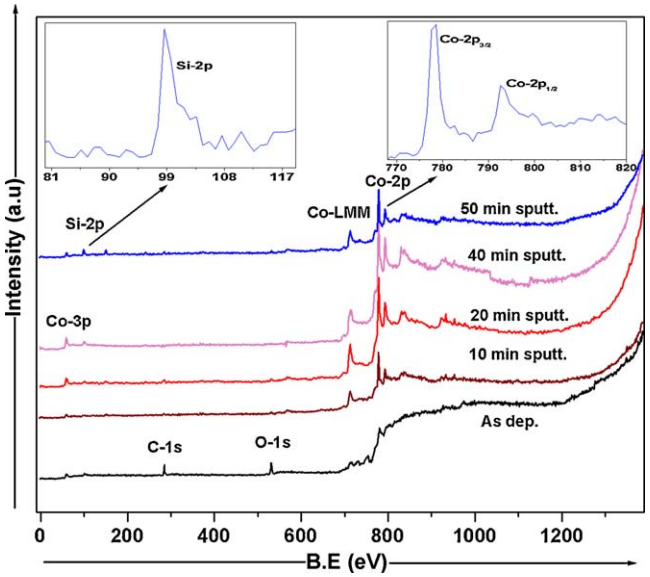

Fig. 1. Survey scans of as deposited Co (400 Å)/Si film. Insets show Si-2p and Co-2p peaks after 50 min sputtering.