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Silicide phases formation in Co/c-Si and Co/a-Si systems during thermal annealing

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ABSTRACT

The effect of the interface in cobalt–silicon bilayers on the silicide phase formation and microstructure has been investigated. Thin cobalt films were deposited by electron beam evaporation to a thickness of 50 nm on crystalline silicon (c-Si) or silicon with pre-amorphized surface (a-Si). After deposition one set of samples was annealed for 2 h at 200, 300, 400, 500, 600 and 700 °C. Another set of samples was irradiated with 400 keV Xe^+ ions and then annealed at the same temperatures. Phase transitions were investigated with Rutherford backscattering spectroscopy, X-ray diffraction and cross-sectional transmission electron microscopy. No silicide formation was observed up to 400 °C, for both non-irradiated and ion-irradiated samples. When increasing the annealing temperature, the non-irradiated and irradiated Co/c-Si samples showed a similar behaviour: at 500 °C, CoSi appeared as the dominant silicide, followed by the formation of $CoSi_2$ at 600 and 700 °C. In the case of non-irradiated Co/a-Si samples, no silicide formation occurred up to 700 °C, while irradiated samples with pre-amorphized substrate (Co/a-Si) showed a phase sequence similar to that in the Co/c-Si system. The observed phase transitions are found to be consistent with predictions of the effective heat of formation model.

1. Introduction

Metal silicides as intermetallic compounds between metals and silicon have interesting physical properties and are widely used for many applications. Good thermal stability, low electrical resistivity and compatibility with silicon processing technology have made them good materials for use in electronics, photovoltaics and thermoelectrics [1–5]. The compound of $CoSi_2$ is a material of choice for contact source, drain and gate areas in complementary metal-oxide-semiconductor devices. Recently, silicide nanostructures have attracted increasing interest for nanoscale device applications.

Thin silicide films have been tailored by ion bombardment of layered structures as well as by physical or chemical vapour co-deposition, pulsed laser deposition, and other thin film deposition methods [6–8]. Rules concerning phase formation to be expected have been established. Walser and Bené [9] stated that the first phase formed in binary diffusion couples is the most stable congruently melting compound adjacent to the lowest eutectic temperature in the phase diagram. A fundamental approach for phase formation was developed by Pretorius [10–12] in terms of the effective heat of formation (EHF) model. By choosing the effective concentration of the reaction to be that of the composition of the lowest eutectic (or liquidus minimum), the EHF model has been successfully used to explain silicide phase formation sequences in many binary metal-silicon thin film systems. It was reported that the first crystalline silicide to be formed is Co_2Si, when cobalt is deposited upon silicon and annealed [13–15]. Holloway found that both Co_2Si and CoSi form simultaneously [16], while Nathan [17] and Miura [18,19] reported CoSi the first crystalline silicide to be formed. Hence, there remain uncertainties concerning the phase evolution in Co/Si couples.

A second motivation was to investigate in what way pre-amorphization of the Si wafers, or ion beam irradiation of the couples before annealing may affect the phase formation process. For instance, Si pre-amorphization is important in semiconductor processing, to produce ultra-shallow junctions. Such treatment induces amorphization and sputtering of contaminants from the Si surface. In this context, the effect of a 1 keV Ar^+ ion pre-implantation in the Si substrates was studied.

This study grew out from our previous work on the Co/Si system [20,21]. There, we had reported that interface mixing of 30–55 nm Co films on Si with Xe^+ ions depends on whether crystalline and pre-amorphizated Si wafers were used. In the present work we highlight the competition between annealing and ion-beam treatment of Co/Si couples with regard to the silicide phase formation sequences and microstructure. This is an extension of our previous

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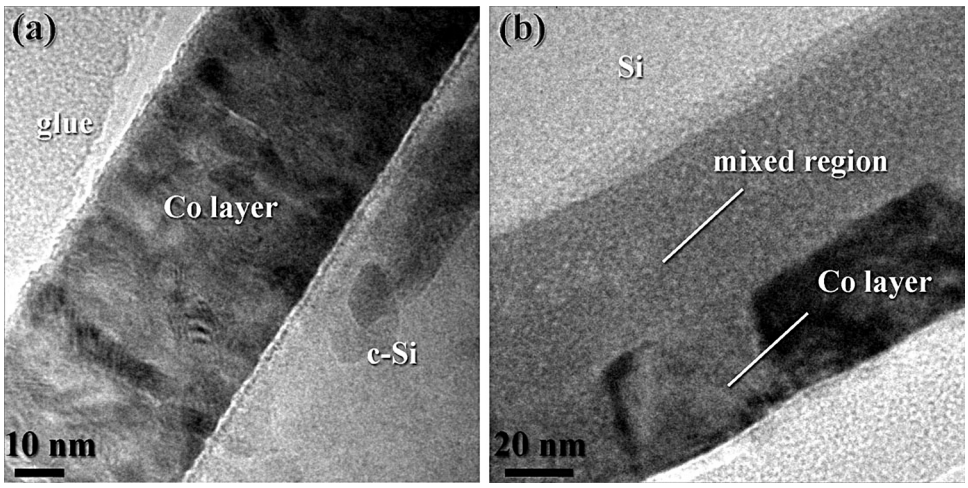

Fig. 1. Cross-sectional TEM images of Co/c-Si system: (a) of as deposited layer; (b) of a sample irradiated with Xe^+ ions to 2×10^{16} ions/cm^2.

work to the case of silicide phase sequences dependences on the substrate structure (c-Si or a-Si). We find that a-Si layer may play important role in interfacial reactions between Co and Si atoms. We show that the interdiffusion and reaction rate of Co and Si can be controlled through thermal treatments and interface structures (c-Si or a-Si). We find that non-irradiated Co/a-Si system is thermally stable up to 700 °C. In this context, our results contribute to better understanding of interfacial reactions occurring at Co/c-Si and Co/a-Si interfaces.

2. Experimental

The Co/Si bilayers used in the present experiments were prepared by electron beam evaporation by means of the thin film deposition facility at VINČA. The substrates used in this experiment were crystalline and pre-amorphized Si(100) wafers. The silicon wafers were cleaned in an HF solution and in de-ionized water before being mounted into the vacuum evaporation chamber. One set of samples, labelled Co/c-Si, was prepared by direct deposition of Co thin films on as-mounted crystalline Si substrates. In the case of another set of samples, labelled Co/a-Si, the Si substrates were bombarded with 1 keV Ar^+ ions, followed by an immediate deposition of Co. The Co films were deposited to a thickness of 50 nm, at room temperature, at an average deposition rate of 0.1 nm/s and a pressure of 1×10^{-4} Pa. An important fact for Co/a-Si samples is that the Ar-treated substrates were not exposed to air, thus providing a clean layer/substrate interface. The projected range of 1 keV Ar^+ ions in Si is about 3.5 nm and the sputtering yield 0.8(3) Si-atom/ion. Irradiation fluence of 1 keV Ar^+ ions was 2×10^{17} ions/cm^2. Consequently, a few nanometer thick amorphous layer was formed on the Si surface. Several samples of both types were then irradiated with 400 keV Xe^+ ions to a fluence of 2×10^{16} ions/cm^2. The chosen energy ensured that the most of the ions passed through the Co film and stopped deep into the substrate, with the maximum energy deposited near the Co/Si interface. According to Monte Carlo SRIM 2003 code [22] calculations, the mean projected range of 400 keV Xe^+ ions lies at 80 nm, with a large full width at half maximum of 135 nm.

The annealing of the irradiated and non-irradiated films was performed in a tube furnace, under a vacuum of some 10^{-6} Pa. The annealing temperatures were 200, 300, 400, 500, 600 and 700 °C and the annealing time was kept constant at 2 h. During the heating process the samples were inserted in the hot region only after the chosen temperature was reached. Also, after the annealing period the samples were moved to a colder region of the tube until they were cooled down to the room temperature.

The depth distribution of components was analysed by Rutherford backscattering spectroscopy (RBS), with the 900 keV He^{2+} ions provided by the Göttingen IONAS accelerator [23] and two Si surface-barrier detectors positioned at 165° to the beam. The experimental spectra from both detectors were fitted with the WiNDF code [24]. The evolution of phases during annealing was determined by X-ray diffraction (XRD) by means of a PHILIPS 1059 diffractometer. The spectra were taken with the CuKα radiation in the 2θ angular range between 40° and 60°. Microstructural analyses of samples were performed by cross-sectional transmission electron microscopy (XTEM), using a PHILIPS CM30 microscope operated at 300 kV. In order to investigate the structure of crystalline regions, image analyses by fast Fourier transformation (FFT) were also carried out. The specimens for cross-sectional examination were prepared by Ar^+ ion beam milling on a Gattan PIPS-691 ion-miller.

3. Results and discussion

3.1. Co/c-Si bilayers

This section refers to the results obtained for the systems with crystalline Si substrates, both non-irradiated and irradiated with 400 keV Xe^+ ions. The interface structures before and after Xe^+ irradiation, as seen by TEM, are presented in Fig. 1. The image of the as-deposited sample (a) shows a sharp interface between the Co layer and Si substrate. Analysis of an irradiated sample (b) indicates the presence of ~50 nm wide intermixed layer between the crystalline Si and non-reacted Co.

Information about atomic transport across the interface during thermal annealing was obtained from RBS analysis. Fig. 2 shows the Co and Si concentration profiles in Co/c-Si layers, as deduced by means of the WiNDF from the RBS spectra taken after deposition and after annealing at 200, 300, 400, 500, 600 and 700 °C. The RBS spectra taken from samples annealed at 200–400 °C showed no changes in concentration profiles of the elements as compared to the as deposited sample. Changes in the spectra are visible at 500 °C and become more pronounced at 600 and 700 °C. Annealing at these temperatures obviously provides conditions for the diffusion through the Co/Si interface: Co and Si migrate towards each other and form fairly homogeneous intermixed layers; the Co:Si atomic ratio is 1:1 at 500 °C and 1:2 at 600 and 700 °C, respectively.