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Silicide formation in Co/Si system investigated by depth-resolved positron annihilation and X-ray diffraction

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Abstract

The transformation of Co/Si to $CoSi_2$/Si in the temperature range of 300–1170 K has been investigated using depth-resolved positron annihilation and Glancing incidence X-ray diffraction (GIXRD). The different silicide phases formed are identified from the experimental positron annihilation characteristics, which are consistent with the GIXRD results. The present study clearly indicates the absence of vacancy defects in the silicide overlayer.

Keywords: Cobalt silicides; Positron spectroscopy; X-ray diffraction

1. Introduction

Study of metal silicides has been a topic of intense basic and technological interest because of their potential applications in semiconductor industry as Schottky barriers, gates, Ohmic contacts, etc. [1,2]. The effect of silicide formation on the generation and the removal of defects is an important issue for better understanding of the mechanism concerning silicide formation. Wen et al. [3], through electrical measurements, reported that the implantation induced interstitials in Si were totally eliminated through the formation of $TiSi_2$ by the injection of vacancies. Similarly, silicidation reactions of metals on Si implanted with various species were also investigated [4] and it was found that the complete annihilation of implantation induced defects depends critically on the distance between the silicide/Si interface, the location of the original amorphous/crystalline interface, the annealing temperature, time etc. Thus, it is important to study the defects and their influence on silicidation using a defect characterization tool together with a complementary structural or phase characterization technique. In this paper, we report the results of depth-resolved positron annihilation spectroscopy (PAS), which has been used to investigate the formation of silicide phases in Co/Si system as well as to probe the presence or absence of vacancy defects consequent to silicide phase formation. Glancing incidence X-ray diffraction (GIXRD) has been used to obtain corroborative evidence for the silicide phases.

2. Experimental

Pure Co (99.99%) was vapor-deposited onto Si (100) wafer at room temperature using a resistive evaporation technique in a vacuum of 1×10^{-6} Torr. Prior to the deposition, the substrate was cleaned using the standard HF acid etching procedure, followed by an in-situ Ar-ion sputtering to remove the native oxide layer. The thickness of the as-deposited Co film was estimated to be ~90 nm from the DEKTAK measurement and 95 ± 10 nm from the Rutherford backscattering spectrometry (RBS). The wafer thus obtained was cut into smaller pieces and annealed in the temperature range 370–1170 K in steps of 100 K for a duration of 1 h each in a vacuum of 1×10^{-6} Torr. Depth-resolved positron annihilation measurements were carried out at room temperature on the annealed Co/Si samples

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using a magnetically guided positron beam system [5]. By varying the positron beam energy (E_p) from 200 eV to 20 keV, positrons can be implanted at selective depth regions of the sample. The positrons so implanted get thermalized and annihilate with the electrons of the sample giving out 511 keV γ-rays. The Doppler broadened 511 keV γ-ray spectrum is recorded using a HPGe detector, having an energy resolution of 1.4 keV at 662 keV. From the measured Doppler broadened spectrum, a defect sensitive lineshape *S*-parameter and a complimentary *W*-parameter are deduced at each E_p. The *S*-parameter is defined as the ratio of counts in the central region (511 ± 1 keV) to the total counts under the photo peak (511 ± 10 keV) and the *W*-parameter is defined as the ratio of counts in the wing regions (507 ± 1 keV) + (515 ± 1 keV) to the total counts (511 ± 10 keV) under the curve [6,7]. While, the *S*-parameter is sensitive to the open volume defects, the *W*-parameter is sensitive to the chemical environment of the annihilation site [7]. To obtain the *S*-parameter values corresponding to the various annihilation states, the experimental $S(E_p)$ curve is analyzed on the basis of the positron diffusion model using the VEPFIT program invoking multilayer fitting [8]. GIXRD measurements were carried out on these samples at a glancing angle of 0.5° using the STOE high resolution X-ray diffractometer.

3. Results and discussion

Fig. 1 shows the variation of the *S*-parameter as a function of positron beam energy, E_p. At low positron energies, the *S*-parameter value is high and characterizes the annihilation of positrons at the surface of the Co overlayer. As the positron energy is increased, the *S*-parameter at first decreases, reaches a minimum value at around 4 keV which characterizes the annihilation of positrons in the Co overlayer. As the positron energy further increases, the *S*-parameter begins to rise and saturates at higher value beyond about 12 keV which is characteristic of the bulk Si value. Upon thermal annealing, the following features are observed: (a) In the temperature range 370–670 K, the *S*-parameter decreases due to the annealing of structural defects in the overlayer. (b) Beyond 670 K, the *S*-parameter increases and approaches a value of 0.563 at 1070 K. (c) At 1170 K, the *S*-parameter drastically increases to ~0.580. It is also observed that the *S* vs. E_p curve has considerably broadened indicating the increase in the thickness of the overlayer. This implies that the silicide formation has certainly taken place. The changes in the *S*-parameter of the overlayer at various annealing stages suggest that PAS is also sensitive to the phase transitions in the Co/Si system.

The silicide phases are identified by comparing the experimental *S*–*W* coordinates of the overlayer with the calculated *S*–*W* coordinates of the silicide phases, namely, Co_2Si, CoSi and $CoSi_2$. If we assume that the *S* and *W* parameters do not depend on the crystal structure and the lattice constants of the material, then the *S* or *W* value of a silicide phase is equal to the weighted averages of the *S* or *W* parameter of the constituents in the bi-atomic material [9]. For co-existence of more than a single phase, the effective *S* or *W* parameter is the average of *S* or *W* parameter of the individual silicide phases. Fig. 2 shows the evolution of the experimental *S*–*W* coordinate of the overlayer as a function of annealing temperature. This is done by taking an average of the *S* and *W* values between 3 and 5 keV (around the minimum at 4 keV) for the 300–1070 K temperature range and between 1 and 5 keV for 1170 K annealed sample. As the annealing temperature is increased, the *S*–*W* coordinate decreases up to about 670 K indicating the

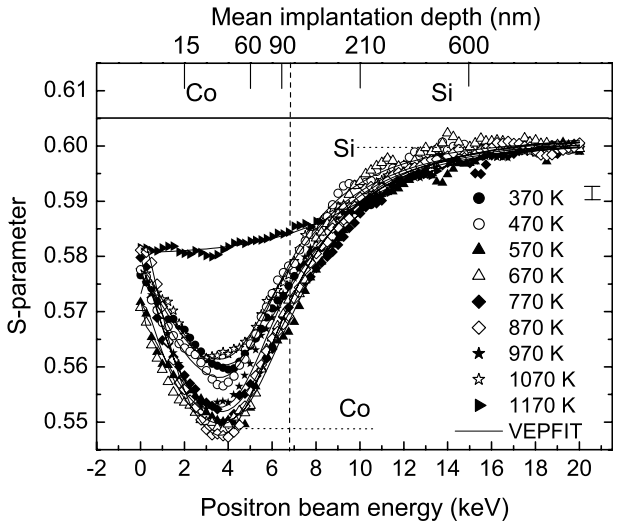

Fig. 1. *S*-parameter vs. positron beam energy curves for the Co/Si system. The mean implantation depth of the positron beam is shown on the top axis. The vertical dashed line corresponds to the location of the original interface. Experimental *S*-parameter values of Co and Si are shown by horizontal lines. The solid line through the data points is a result of the VEPFIT analysis.

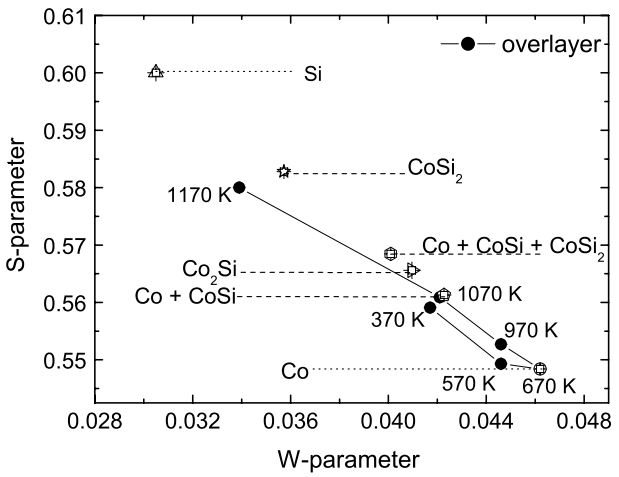

Fig. 2. *S*–*W* correlation plot of the overlayer for various annealing temperatures. The closed symbols represent the experimental *S*–*W* coordinates and the open symbols represent the calculated *S*–*W* coordinates. Experimental values for pure Co and Si are also shown. The solid line through the data points is a guide to the eye.

annealing of structural defects in the overlayer. The *S*–*W* coordinate at 670 K matches with the *S*–*W* coordinate of the annealed Co state. Beyond 670 K, the *S*–*W* coordinate increases. The increase in the *S*–*W* coordinate between 670 and 1070 K is attributed to intermixing of Co and Si across the interface, prior to silicide formation. At 1070 K, the *S*–*W* coordinate matches with the *S*–*W* coordinate of the overlayer comprising of Co and CoSi suggesting the onset of silicide phase formation. For 1170 K, the experimental *S*–*W* coordinate is very close to the calculated *S*–*W* coordinate of $CoSi_2$ indicating that there is a complete conversion to $CoSi_2$ at this temperature. Since, the *S*–*W* coordinate of the overlayer matches well with the estimated *S*-*W* coordinate of the silicide phase, it is an indication that the silicide overlayer is free from the vacancy defects.

Fig. 3 shows the GIXRD spectra of Co/Si samples at selected annealing temperatures. As can be seen, only Co lines are present until about 970 K indicating that no silicide formation has taken place but intermixing across the interface cannot be ruled out. At 1070 K, there are prominent Co and CoSi lines and less intense lines due to $CoSi_2$ phase. At 1170 K, only $CoSi_2$ lines are present. This indicates the complete conversion to $CoSi_2$ phase. The identification of the silicide phases at 1070 K and 1170 K compares well with that identified from the *S*–*W* correlation plot.

Furthermore, the experimental *S* vs. E_p curves were analyzed using the VEPFIT program by assuming a two-layer model comprising of the overlayer and the substrate region at various temperature regimes i.e., Co and Si between 370 K and 970 K, CoSi and Si at 1070 K, $CoSi_2$ and Si at 1170 K. From the VEPFIT analysis, the thickness of the Co overlayer was found to be $\sim 80 \pm 20$ nm in the temperature range 370–970 K which compares favourably with

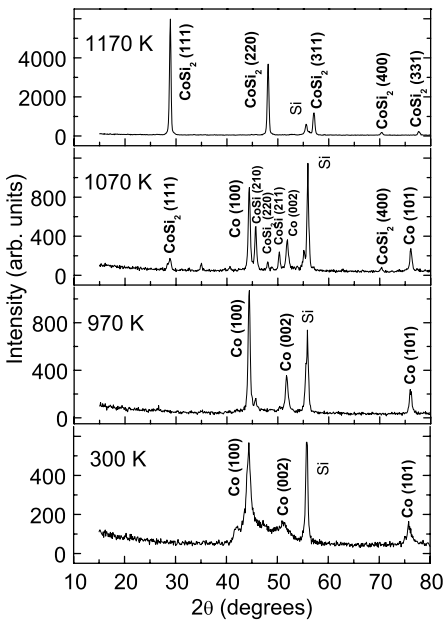

Fig. 3. GIXRD spectra of Co/Si samples at selected annealing temperatures. Peaks due to Co, CoSi, $CoSi_2$ and Si lines are marked.

DEKTAK and RBS estimates. For 1070 K and 1170 K annealed sample, the thickness of the overlayer increased to 95 nm and 400 nm, respectively. The thickness of $CoSi_2$ overlayer at 1170 K is consistent with that calculated for a given thickness of Co to form $CoSi_2$ [1]. The VEPFIT deduced positron diffusion length in the overlayer ranges between 8 and 15 nm in the temperature range 370–970 K. A possible reason for observing a smaller positron diffusion length in the overlayer would be due to the small grain size of the Co microcrystals. On the other hand, the diffusion length of positrons in the $CoSi_2$ overlayer turns out to be $\sim$200 nm. Taking into account, the positron diffusion coefficient [9] to be 2.9 cm^2 s^{-1} and the positron lifetime of $CoSi_2$ as 155 ps [10], the positron diffusion length can be estimated to be $\sim$210 nm, which compares favorably with the present experimental value. This indicates that the $CoSi_2$ overlayer is devoid of vacancy defects. It may also be pointed out that the estimated *S*–*W* coordinate of $CoSi_2$ compares well with the experimental value signifying that the $CoSi_2$ overlayer is devoid of vacancy defects. Thus, it is inferred that no vacancy defects are present in the silicide overlayer as well as at the substrate end of the interface. It may be pointed out that vacancy defects are created at the interface consequent to diffusion of either the metal or the silicon atoms [11,12]. If Si is the dominant diffusing species, vacancy defects are created at the interface as well as the substrate region, as observed in the Pd/Si system [13]. On the other hand, if metal is the dominant diffusing species, then no vacancy defects are created at the interface or at the substrate region, which is the case for Ni/Si system [14]. Our recent Rutherford backscattering spectrometry(RBS) studies on the same Co/Si samples [15] have indicated that Co elemental profile gets more broadened as compared to Si elemental profile consequent to the silicidation, suggesting that Co is the fast diffusing species, which is consistent with the present observation of absence of vacancy defects.

4. Conclusions

Co/Si samples subjected to various annealing temperatures have been investigated using positron beam based Doppler *S*-parameter and GIXRD measurements. Silicide formation begins around 1070 K with the overlayer comprising of Co, CoSi and small traces of $CoSi_2$. At 1170 K, there is a complete conversion to the $CoSi_2$ phase. The different silicide phases identified using the *S*-*W* correlation plot and the GIXRD are consistent with each other. Further, from the analysis of the positron annihilation data in terms of the *S*-*W* coordinates and the diffusion lengths, it is inferred that no vacancy defects are present in the interface as well as in the silicide overlayer.

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