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Probing Co/Si Interface by Raman Spectroscopy

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The characteristics of the metal on the Si surface have been extensively explored due to the industrial relevance of transition metal silicide in integrated circuit technology and scientific interest in the influence of the adlayer on Si substrate reconstruction and heterodiffusion. Even though the interaction of Co with Si is not entirely understood, there are still disagreements over the nature of the Co/Si system. Several problems remain unsolved, including predictions of the phase that would precipitate among the several phases of the Co/Si system as a function of film thickness and temperature. Therefore, in order to understand the same, cobalt (Co) thin films of thicknesses 10, 40, and 100 nm were produced by electron beam physical vapor on silicon substrates. After deposition, the samples were further annealed at 200, 300, and 400 °C for 2 h. Micro-Raman spectroscopy (due to its non-destructive nature) was used to analyze the chemical composition and silicide formation at the interface as a result of the thickness and temperature variation in as-deposited and annealed samples. The results demonstrate that the grown films are of high quality and devoid of impurities. Studies reveal that silicide is formed during deposition at the interface, and the development of a new band at 1550 cm^{-1} as a result of annealing shows structural transformation from CoSi to $CoSi_2$, which strengthens further at higher annealing temperatures.

Keywords: Raman scattering, Thin films, Nanostructures.

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1. INTRODUCTION

The interface between two layers of different materials with similar/different layer parameters opens up an incalculable number of possibilities. By choosing suitable growth conditions, substrates and temperatures, one can tailor the physical properties of these structures. In recent years, the experimental and theoretical research of metal/semiconductor interfaces has witnessed rapid growth. In particular, due to the technological importance of transition metal silicide in integrated circuit technology and scientific interest in the effect of the adlayer on Si substrate reconstruction and heterodiffusion, the properties of the metal on the Si surface have been widely studied [1-3]. In this respect, the interface between Co and Si has been extensively studied due to its low resistivity, high thermal stability, minimum lattice mismatch with silicon, sharp interface (ideal for making Schottky barriers), and compatible handing out treatment [4, 5]. In addition to this, cobalt and Co-based thin-film structures have attracted large interest in nanoscale device applications and offer tremendous opportunities for designing futuristic and innovative magneto-transport devices [4-7]. However, any structural instability at the Co/Si interface can significantly limit the spin injection efficiency [8, 9]. Due to the negative heat of mixing at elevated temperatures, silicon involves the diffusion of metal, silicon, or both species across the interface [10, 11]. $CoSi_2$ is often used as gates and connections between all-metal silicide because it has low resistance, a lattice structure that works well with silicon, and can be used as a conductive and magnetic material in many electronic applications. But the main problem with making these kinds of devices is that a lot of the semiconductor elements in the substrate end up in the overlayer. This alters the properties of the material deposited in a significant way [12, 13].

In the recent past, several techniques, namely X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Rutherford backscattering (RBS), etc. have been utilized to characterize the Co/Si interface and the chemical composition of different phases of Co silicide as a function of thickness and temperature. As compared to the above analytical methods, Raman spectroscopy is more advantageous, since it is not only a powerful tool for material research; it is non-destructive and does not require any special arrangement for sample preparation [14]. But so far, not many Raman studies have been done on co-silicide [15, 16]. This could be because silicide does not have any lattice vibrational modes (making it "Raman inactive") or because the vibrational frequencies are too low to be seen.

The interaction of Co with Si is not fully understood yet, and controversies still exist about the nature of the Co/Si system. Various questions are still unanswered, such as the predictions of the phase, which will precipitate among the different phases that exist for the Co/Si system, how thick the silicide layer formed at the interface will be, and how it will vary with film thickness. In addition to this, these properties are also very susceptible to degradation with temperature due to the significant intermixing of the underlying substrate element into the over layer [17, 18]. Using micro-Raman spectroscopy, the goal of this study is to find out how thickness and temperature affect the Co/Si interface.

2. EXPERIMENTAL DETAILS

Using the electron beam physical vapor deposition method, cobalt thin films with thicknesses of 10, 40, and 100 nm were formed on silicon substrates. Prior to the depositions, the deposition chamber was evacuated to a

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low pressure to allow electrons to travel from the source to the evaporation material. Substrates were washed with soap solution first, then rinsed with distilled water, and finally with acetone solution before deposition. After deposition, four segments from each silicon wafer were cut and annealed independently for 2 h at temperatures of 200, 300, and 400 °C. On an InVia Renishaw micro-Raman microscope, a 514 nm line of Ar laser with a maximum power of 50 mW was used to measure all nine annealed samples and three pure samples.

3. RESULTS AND DISCUSSION

Raman spectroscopy is a non-destructive chemical analysis technique that provides detailed information about the chemical structure, phase, contamination, and impurity. Therefore, to investigate phase formations and characteristics of the Co/Si interface as a function of thickness and temperature, micro-Raman measurements have been taken. All nine annealed samples and three pristine samples underwent micro-Raman spectroscopy studies. Raman spectra for pristine cobalt films of 10, 40, and 100 nm on silicon are displayed in Fig. 1. The spectrograms show four distinct peaks at 517, 938, and 1330 cm^{-1}. Raman active phonon modes from the Si lattice are responsible for the peaks at 517 cm^{-1} and 938 cm^{-1}. The 517 cm^{-1} peak is the first-order Si Raman band and has a high intensity. Moreover, as the thickness of the Co film increases, the intensity of these peaks decreases. In fact, these peaks practically disappear in the case of Co (100 nm) film. The reduction in the intensity of Si bands with increasing Co film thickness from 10 to 100 nm is due to the increased thickness limiting laser penetration and therefore only a weak signal from the Si substrate and more from the Co surface can be detected. One can also see a second peak at a higher frequency (1330 cm^{-1}), which corresponds to the Raman band of silicide and whose intensity increases with increasing Co film thickness rather than decreasing as one would expect for Si bands. Also of interest is the fact that the Co oxide peak reported by F.M. Liu et al. [12] is not present in the current study, indicating that no cobalt oxide was formed during deposition. This is indicative of the high quality of the samples that were prepared.

Fig. 2 depicts a comparison of the Raman spectra of Co placed on Si with a film thickness of 10 nm for as-deposited and samples annealed for 2 h at 200, 300, and 400 °C, respectively. Except for a very small drop in the intensity of peak position, 517 cm^{-1}, no change in the intensity or location of the Raman peaks is noticed as the annealing temperature changes (see the inset of Fig. 2).

Similarly, Fig. 3 displays the Raman spectra of cobalt (40 nm) film deposited on silicon substrate as a function of annealing temperature. In contrast to the earlier Co (10 nm) film, a notable difference (drop) in the intensity has been observed at the peak position, 517 cm^{-1} (see the inset of Fig. 3).

On the other hand, it may be seen in Fig. 4, at a film thickness of 100 nm, the peak intensity at 517 cm^{-1} is extraordinarily low, and the intensity drop is likewise very negligible (Fig. 5) when the annealing temperature increases. Fig. 5 compares the Raman spectra of a Co (100 nm) film as a function of annealing temperature ranging from 400 to 1700 cm^{-1}. Interestingly, it is also

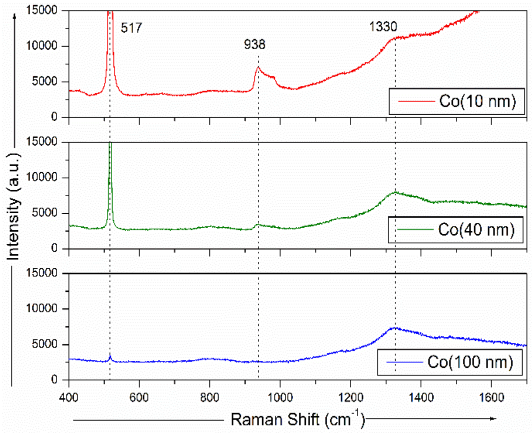

Fig. 1 – Raman spectra of Co film as a function of layer thickness

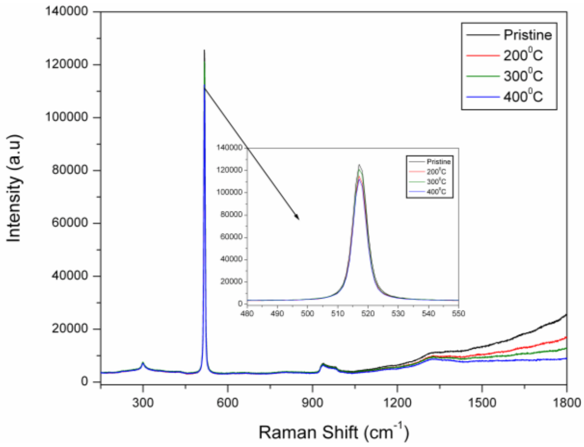

Fig. 2 – Raman spectra of Co (10 nm) film as a function of annealing temperature

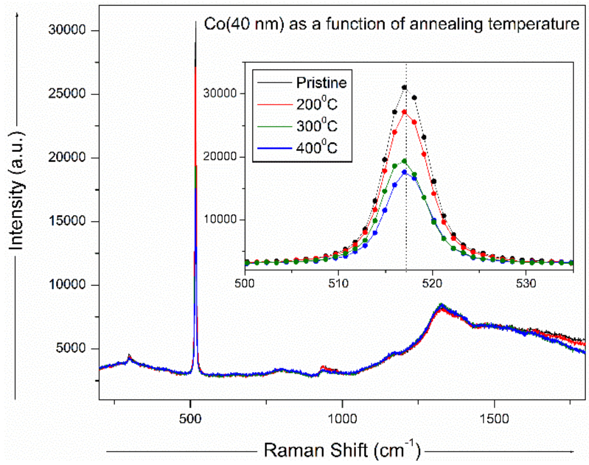

Fig. 3 – Raman spectra of Co (40 nm) film as a function of annealing temperature

visible from the curve that a shoulder-like peak at position 1550 cm^{-1} appears and is notable (in addition to 1330 cm^{-1}, as seen in Fig. 5). Unlike other peaks, the intensity of these peaks at 1550 cm^{-1} and 1330 cm^{-1} increases as the annealing temperature increases. The increase in peak the intensity at 1330 cm^{-1} and the emergence of a new band at 1550 cm^{-1} as a result of annealing suggest the structural transition from CoSi to

$CoSi_2$ at the interface, which improves further at higher annealing temperatures.

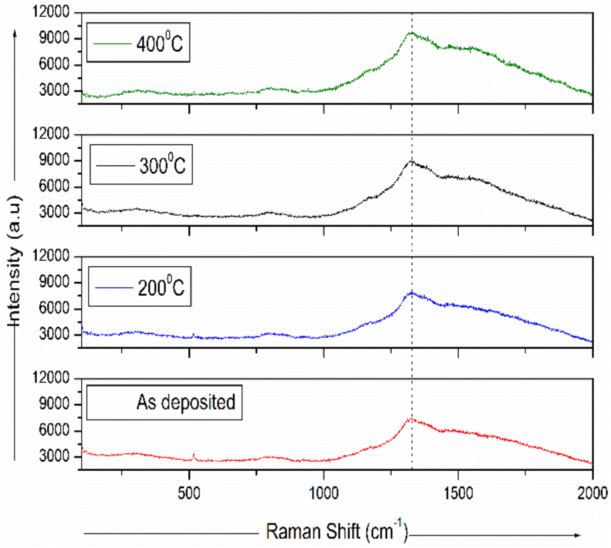

Fig. 4 – Raman spectra of Co (100 nm) film as a function of annealing temperature

4. CONCLUSIONS

A systematic thickness-temperature-driven micro-Raman study was undertaken to learn more about the chemical composition and formation of silicide at the interface of Co film deposited on Si substrate. Based on these investigations, we may draw the following conclusions:

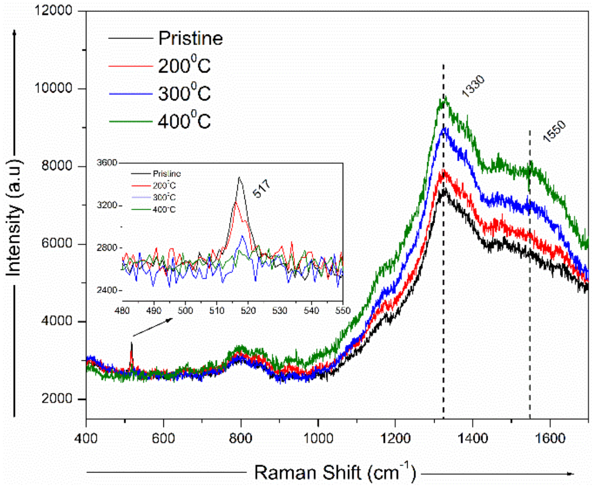

Fig. 5 – Comparison of the Raman spectra of Co (100 nm) film as a function of annealing temperature ranging from 400 to 1700 cm^{-1}

- The grown films are free from impurity.
- Silicide is formed at the interface during deposition.
- At the higher annealing temperature, CoSi undergoes a structural transition that yields $CoSi_2$ as a by-product.

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Зондування інтерфейсу Co/Si за допомогою раманівської спектроскопії

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Характеристики металу на поверхні кремнію були широко досліджені завдяки промисловій значущості силіциду перехідного металу в технології інтегральних схем і науковому інтересу до впливу адсорбованого шару на реконструкцію підкладки кремнію та гетеродифузію. Зважаючи на те, що взаємодія Co з Si не зовсім зрозуміла, все ще існують розбіжності щодо природи системи Co/Si. Кілька проблем залишаються невирішеними, включаючи передбачення фази, яка виділиться серед кількох фаз системи Co/Si як функція товщини плівки та температури. Тому, щоб зрозуміти останнє, тонкі плівки кобальту (Co) товщиною 10, 40 і 100 нм були виготовлені методом електронно-променевого осадження на кремнієві підкладки. Після осадження зразки додатково відпалювали при 200, 300 і 400 °C протягом 2 годин. Мікро-раманівська спектроскопія (через її неруйнівну природу) була використана для аналізу хімічного складу та утворення силіцидів на інтерфейсі в результаті зміни товщини та температури в осаджених і відпалених зразках. Результати демонструють, що вирощені плівки мають високу якість і не містять домішок. Дослідження показують, що силіцид утворюється під час осадження на інтерфейсі, а розвиток нової смуги при 1550 см$^{-1}$ у результаті відпалу свідчить про структурну трансформацію від CoSi до $CoSi_2$, яка ще більше посилюється при вищих температурах відпалу.

Ключові слова: Комбінаційне розсіяння, Тонкі плівки, Наноструктури.