

In-situ formation of Ge-rich SiGe alloy by electron beam evaporation and the effect of post deposition annealing on the energy band gap

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ABSTRACT

We report the synthesis of polycrystalline (*poly*)-SiGe alloy thin films through solid state reaction of Si/Ge multilayer thin films on Si and glass substrates at low temperature of 500 °C. The pristine thin film was deposited using electron beam evaporation with optimized in-situ substrate heating. Our results show the co-existence of amorphous Si (*a*-Si) phase along with the *poly*-SiGe phase in the pristine thin film. The *a*-Si phase was found to subsume into the SiGe phase upon post deposition annealing in the temperature range from 600° to 800 °C. Additionally, dual energy band gaps could be observed in the optical properties of the annealed *poly*-SiGe thin films. The stoichiometric evolution of the pristine thin film and its subsequent effect on the band gap upon annealing are discussed on the basis of diffusion characteristics of Si in *poly*-SiGe.

1. Introduction

For the past several decades, the prime material for absorber layer of solar cells in photovoltaic (PV) industries has been elemental Si, both in its amorphous (*a*-Si) as well as crystalline (*c*-Si) form [1,2]. Si is also the basic material in high performance optoelectronic and microelectronic devices like photodiode, active matrix-LCD, image sensors, integrated electronics [3]. It is largely due to abundance and cost effectiveness in large scale production of Si. However, Si has inherently low absorption co-efficient in the Infra Red (IR) region of the solar spectrum and devices based on Si have low efficiency and light induced degradation due to Staebler-Wronski-Effect [4,5]. Due to these shortcomings, SiGe has been investigated as an alternative to Si for the above applications for past few decades [6]. The attractive properties of SiGe results from the addition of electrically and optically superior Ge that makes the lattice constant and energy band gap tunable in a broad range. SiGe as a result have high absorption co-efficient and its optical response can be improved in the IR region. Hence, particularly for PV industries, the use of SiGe increases the effective absorption of the solar spectrum and increases the efficiency of the thin film solar cell. The use of amorphous SiGe (*a*-SiGe) as absorber material in solar cell is reported to result in the increase of long wavelength response in Quantum Efficiency (QE) up to 950 nm [7]. The longer wavelength response in QE

can be further extended beyond the value reported with *a*-SiGe by using microcrystalline SiGe (*mc*-SiGe) instead of *a*-SiGe [8]. Apart from crystallinity, the spectral response depends on the Ge content in the SiGe alloy. This was demonstrated when Ni et al. [9] reported achieving an spectral response of up to 1300 nm using *mc*-SiGe with a Ge fraction of $\approx 77\%$. Hence, good quality Ge rich *c*-SiGe is desirable for PV applications. Further, the melting temperature T_m of SiGe is lower than Si as it lies between $T_{m(Ge)} = 940^\circ\text{C}$ and $T_{m(Si)} = 1414^\circ\text{C}$ [10]. As such, deposition, crystallization, grain growth and dopant activation in SiGe occur at relatively lower temperature compared to Si and find use in applications where lower thermal budget is desirable. Herein, the synthesis of Ge rich polycrystalline (*poly*)-SiGe at low temperature is challenging. The synthesis methods generally used to achieve *poly*-Si, Ge and SiGe are Solid Phase Crystallization (SPC), laser annealing, electron beam (e-beam) crystallization, Metal Induced Crystallization (MIC), etc [11–15]. Among these techniques, MIC can enable growth of SiGe at the lowest temperature in the range $\sim 150\text{--}400^\circ\text{C}$ [16,17]. However, there is a chance of degradation in semiconducting properties due to metal contamination in MIC process [18]. In contrast, SPC is the simplest and most cost effective method. It does not involve any toxic metals or gas. Using SPC, *a*-SiGe is reported to transform into *poly*-SiGe at 625 °C after annealing for a period of more than 24 h [19]. Earlier, we have reported formation of nanocrystalline (*nc*)-SiGe by ex-situ

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annealing of Ge/Si (111) thin films by e-beam evaporation [20]. No *nc*-SiGe phase could be observed with in-situ substrate heating at 450 °C during deposition. It could be achieved only upon ex-situ annealing at temperature ≥ 600 °C.

In this paper, we report the synthesis of Ge-rich $\text{Si}_x\text{Ge}_{1-x}$ alloy thin film on Si and Corning 0215 glass substrates using e-beam evaporation method at low temperature of 500 °C. With in-situ substrate heating at 500 °C, crystalline $\text{Si}_x\text{Ge}_{1-x}$ phase could be achieved during the sequential evaporation of Si/Ge multilayer thin film on Si and Corning glass substrates. The stoichiometric evolution of the $\text{Si}_x\text{Ge}_{1-x}$ phase along with the optical characteristics upon post deposition isochronal annealing at higher temperatures ranging from 600° to 800 °C is discussed.

2. Experimental

For the present study, thin film samples were prepared by sequential deposition of Ge/Si of 15 nm each with two periods onto cleaned Si (100) and corning glass substrates using e-beam evaporation. Si was chosen as the top layer of the period to prevent loss of Ge due desorption at high temperatures [21,22]. The base pressure in the deposition chamber and the working pressure during deposition were $\sim 10^{-8}$ mbar and $\sim 10^{-7}$ mbar, respectively. The temperatures of the substrates, T_s , were maintained at 500 °C by in-situ heating of the substrate stage and the stage was rotated for film uniformity during the deposition. In the forthcoming discussion, for brevity, the thin film deposited at 500 °C will be hereafter referred to as ‘pristine sample’. Post deposition isochronal annealing of the pristine thin films was performed at annealing temperature T_a , ranging from 600° to 800 °C for 5 h in N_2 ambient. The structural characteristics of all the thin film samples in the present study were investigated using grazing incidence x-ray diffraction (GIXRD) and Raman spectroscopy. The GIXRD measurements were performed with 15.501 keV energy x-rays at 0.3 degree angle of incidence on angle dispersive x-ray diffraction beam line of the Indus-2 Synchrotron facility at RRCAT, Indore. The Raman spectral measurements of all samples in the present study were performed in a Raman microscope (inVia, Renishaw, UK) using green light laser 514.5 nm as the excitation source along with 1800 gr/mm grating and CCD detector. The detailed structural phase information of the thin film sample was further investigated with high resolution transmission electron microscopy (HRTEM) imaging and selected area electron diffraction (SAED). The HRTEM and SAED measurements were performed in a LIBRA 200FE HRTEM, (Carl Zeiss) and the information limit of the HRTEM is 0.13 nm. The surface topography of all the thin films was acquired using Atomic Force Microscope (NT-MDT) in semi-contact mode. Further, the morphology of all the thin film samples were investigated using field emission scanning electron microscope (FESEM, Carl Zeiss Supra 55). The optical characterizations of the thin films were performed in a UV–Vis–NIR spectrophotometer (Hitachi UH4150).

3. Results and discussion

Before getting into the details of our experimental results, a brief mention about the barrier to nucleation of crystalline SiGe alloy in Si/Ge multilayer thin film is relevant. Among other thermodynamic considerations, this barrier primarily arises from energy considerations required to break the covalent Ge–Ge (1.9 eV) and Si–Si (2.3 eV) bonds from their respective elemental matrix and undergo structural rearrangement into the alloy phase by forming covalent Si–Ge bonds [23]. This barrier is circumvented at $T_s \approx 500$ °C as Ge atoms become mobile enough to crystallize into *poly*-Ge and mobility of the Si *ad*atoms arriving at the film's surface gets enhanced because of the supplied thermal energy [13]. The GIXRD patterns of the pristine and the annealed thin film samples are shown in Fig. 1. The formation of *poly*-SiGe phase in the pristine thin film can be inferred from the XRD peaks observed at interplanar spacing (d) values ~ 3.23 , 1.97, 1.68 and

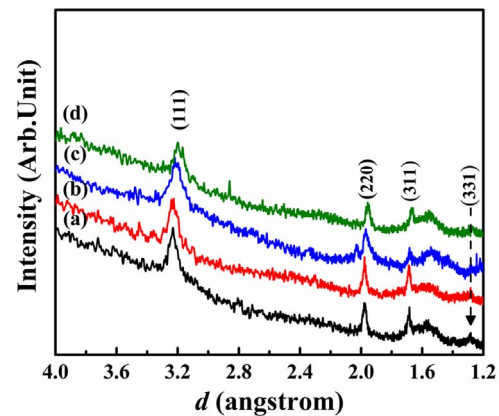


Fig. 1. GIXRD pattern of (a) pristine thin film; and after annealing the pristine thin film at (b) 600 °C; (c) 700 °C and (d) 800 °C for 5 h.

1.28 Å. These peaks correspond to the SiGe (111), SiGe (220), SiGe (311) and SiGe (331) planes, respectively. Moreover, peaks corresponding to *poly*-Ge and *poly*-Si phases are absent in the GIXRD pattern of the pristine thin film. Herein, it may be noted that the crystallization temperature of amorphous bulk Ge ($T_{c(a-Ge)}$) and amorphous bulk Si ($T_{c(a-Si)}$) are ~ 500 °C and 700 °C, respectively [13]. The absence of peaks corresponding to *poly*-Ge shows that all the elemental Ge actively participates in the alloying process. Although peaks corresponding to *poly*-Si are also absent in the pattern, the same cannot be inferred for elemental Si because it is still possible that some fraction of elemental Si continue to remain in amorphous state owing to its higher $T_{c(a-Si)}$. Consequently, the SiGe thin film that forms is expected to be Ge-rich. Intricate details like the presence of *a*-Si phase can be revealed by an investigation with structural characterization techniques which is both complementary to XRD and is also sensitive to amorphous phases [24]. Further, the XRD peaks corresponding to *poly*-SiGe phase {(111) & (220) planes} shows slight broadening along with a small shift in the peak positions toward lower d values, upon annealing the pristine sample at higher T_a (see Fig. 1). The observed broadening is intriguing because when a polycrystalline sample is annealed at higher T_a , the crystalline order in the sample generally improves through annealing of various defects and re-crystallization. Disruption of existing long range crystalline order in a sample can occur only in a non-equilibrium process like ion beam irradiation and not in a thermal annealing process. Phase segregation at higher T_a as a factor for the observed broadening can be also ruled out as Si and Ge are completely miscible system. The most probable explanation for the observed broadening in the XRD peaks is nucleation of new additional $\text{Si}_x\text{Ge}_{1-x}$ phase with composition different from that of the pristine *poly*- $\text{Si}_x\text{Ge}_{1-x}$ thin film. Moreover, the observed shift in XRD peak positions also indicates a stoichiometric change at higher T_a according to Vegard's law [25]. This inference will be corroborated with other experimental observations and are discussed elaborately later in the article.

Raman measurements were performed in the samples to gain further insight into the alloying process. The Raman spectra acquired from the pristine and the annealed thin films are shown in Fig. 2. Apart from the Raman peak at $\sim 521 \text{ cm}^{-1}$ which arises from the Si substrate [26], the Raman spectra of the pristine thin film exhibit three main peaks centered at ~ 291.6 , 398.8 and 459 cm^{-1} . These three peaks corresponds to the vibration modes of Ge–Ge, Si–Ge and Si–Si covalent bonds, respectively [27,28]. The peak at $\sim 398.8 \text{ cm}^{-1}$ confirms the formation of SiGe phase in the pristine thin film. We can also note that the SiGe peak exhibit a small asymmetry in the profile towards the lower energy side. The phonon mode of Si–Ge arises due to the localized vibration of the lighter Si atoms that are bonded to much heavier Ge atoms [29]. Consequently, the peak from Si atoms that are co-ordinated with four Ge atoms (Si- Ge_4) appears at lower energy than from Si atoms that are

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