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Aluminum-induced crystallization of amorphous silicon–germanium thin films
Stabilization of amorphous structure in silicon thin film by adding germanium

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The stabilization of the amorphous structure in amorphous silicon film by adding Ge atoms was studied using Raman spectroscopy. Amorphous Si$_{1-x}$Ge$_x$ ($x = 0.0, 0.03, 0.14, and 0.27$) films were deposited on glass substrates from electron beam evaporation sources and annealed in N$_2$ atmosphere. The change in the amorphous states and the phase transition from amorphous to crystalline were characterized using the TO, LO, and LA phonons in the Raman spectra. The temperature of the transition from the amorphous phase to the crystalline phase was higher for the a-Si$_{1-x}$Ge$_x$ ($x = 0.03, 0.14$) films, and the crystallization was hindered. The reason why the addition of a suitable quantity of Ge atoms into the three-dimensional amorphous silicon network stabilizes its amorphous structure is discussed based on the changes in the Raman signals of the TO, LO, and LA phonons during annealing. The characteristic bond length of the Ge atoms allows them to stabilize the random network of the amorphous Si composed of quasi-tetrahedral Si units, and obstruct its rearrangement. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4922670]

I. INTRODUCTION

Amorphous silicon (a-Si), which is a tetrahedral amorphous semiconductor, is an industrially important thin film material used for thin film transistor (TFT) liquid crystal displays and solar cells. Amorphous silicon TFTs are mainly applied in monitors and televisions. Polycrystalline silicon film can be made by annealing the a-Si film and is applied in high-resolution TFT liquid crystal displays, such as for mobile and smart phones. The characteristic properties of polycrystalline silicon are influenced by its amorphous structure before crystallization.

The continuous random network model is a well-known model used to describe the atomic structure of a-Si.$^1$ The structure has local short-range order, despite having no long-range order or translational symmetry. It has already been reported that this amorphous structure is not stable like that of a crystal but is a metastable state, and has a melting point and a relaxed structure, as determined by colorimetric study of its crystallization.$^{2,4}$ Using differential scan thermometric analysis, Donovan et al.$^2$ determined that the melting point of a-Si is lower than that of crystalline silicon, and reported that the melting point is dependent on the relaxed structure of the a-Si. Moreover, they predicted that the melting point would be decreased for an insufficiently relaxed amorphous state. Roorda et al.$^{3,4}$ reported that the amorphous structure of silicon film deposited at room temperature is not relaxed, but is in a high-energy state, and is relaxed well by annealing at a temperature between 500°C and 800°C. The corresponding structural relaxation process is considered to arise from a change in the short-range order owing to the annihilation of defects and the reduction of variation in the Si-Si bond angle.

In the case of fabrication of polycrystalline silicon from amorphous silicon by annealing, it is reported that the crystallization temperature is lowered by the addition of Ge atoms.$^5$–$^9$ Polycrystalline silicon-germanium thin films have been expected to improve TFT characteristics$^{10,12}$ because of their superior properties such as large grain size and high mobility. Because Si and Ge have different characteristic bond lengths, the Si-Si bond is strained by the presence of Ge atoms and the resulting strained Si crystal gives rise to the high mobility.

In this paper, we investigate the stabilization of the amorphous structure of a-Si by adding Ge atoms, which is a group IV element and has the same network structure as that of a-Si. To investigate the stability, we observed the change in the Raman spectra before and after annealing at 600°C or 800°C. These two annealing temperatures correspond to the limits of the characteristic temperature ranges reported to cause Si-Si bond rearrangement during the solid phase epitaxial growth on Si (111) substrate.$^{13,16}$

II. EXPERIMENTAL

Amorphous Si$_{1-x}$Ge$_x$ ($x = 0.0, 0.03, 0.14, and 0.27$) films were deposited on glass substrates (Corning 1737) at room temperature from an electron beam evaporation source after cleaning by irradiation with excimer ultraviolet light. The thickness of the film was controlled at 50 nm using a quartz thickness monitor. The pressure during the film growth was kept under 1 x 10$^{-4}$Pa, and the substrate was heated by a few tens of degrees Celsius by the radiation from the evaporation source. To prepare the evaporation source, silicon pellets (99.999% in purity) and germanium powder (99.9%) were measured out to the desired composition and fused into a SiGe compound pellet by electron beam irradiation under vacuum. The Si$_{1-x}$Ge$_x$ films were deposited from the SiGe pellets using a deposition rate of 2 nm/min. The ratio of Ge and Si in each deposited film was measured by X-ray photoelectron spectroscopy (XPS), after cleaning the film by Ar ion sputtering to remove surface organic contaminations and...
oxide layer. An Al-Kα (1486.4 eV) X-ray source was used in the XPS measurement, and the photoelectrons emitted from the sample surface were detected at an escape angle of 55° from the surface normal. Si$_{1-x}$Ge$_x$ films having Ge concentrations of 0, 3, 14, and 27 at. % (x = 0.0, 0.03, 0.14, and 0.27) were chosen as the samples for investigating the stability of the amorphous states.

Organic contamination was observed on the surface of the samples by XPS. The concentration of carbon in the films was below the detection limit of the XPS after the Ar ion sputtering. After the sputtering, oxygen was observed, but Si-O phonons were not detected from the films during the Raman spectroscopy. The O signal in the XPS was caused by intermixing of the surface oxide layer during the Ar ion sputtering.

The as-deposited Si$_{1-x}$Ge$_x$ films were annealed at $T_a = 600$ °C or 800 °C for 90 min using a thermal annealing apparatus at a heating rate of 50 °C/s in 0.5 atm N$_2$ gas. After the annealing, the structural change in the Si$_{1-x}$Ge$_x$ films was evaluated with a laser Raman microscope, using an Ar laser (514 nm) as the excitation source and an exposure time of 20 min.

III. RESULTS AND DISCUSSION

A. Influence of Ge atoms on the crystallization of Si$_{1-x}$Ge$_x$ films

To investigate the influence of Ge atoms on the crystallization of the a-Si film, Raman spectra of the obtained Si$_{1-x}$Ge$_x$ films were measured after the samples were annealed at $T_a = 800$ °C for 90 min, because the crystallization of a-Si starts at about 800 °C. Figure 1 shows the Raman spectra of the annealed Si$_{1-x}$Ge$_x$ films with x = 0, 0.03, 0.14, and 0.27.

In the spectrum of the Si$_{1-x}$Ge$_x$ film with x = 0, the Raman peak observed between 510 and 520 cm$^{-1}$ is assigned to the Si-Si phonon mode in the polycrystalline silicon. The weak and broadened bands observed between 200 and 500 cm$^{-1}$, were assigned to TO, LO, and LA phonons originating from the amorphous silicon. It is clear that the amorphous undoped silicon film was partly crystallized by the annealing at 800 °C.

In contrast, in the case of Si$_{1-x}$Ge$_x$ films with x = 0.03 and 0.14, the Raman peak of polycrystalline silicon was not observed. This means that these Si$_{1-x}$Ge$_x$ films were not crystallized by the annealing at 800 °C. The broad Raman bands resulting from the amorphous state were observed between 200 and 500 cm$^{-1}$. These bands assigned to the TO, LO, and LA phonons from amorphous silicon indicate that the amorphous state of the x = 0.03 and 0.14 film was maintained after the annealing at 800 °C.

When the Ge concentration was increased to x = 0.27, a Raman peak resulting from polycrystalline silicon was observed between 500 and 515 cm$^{-1}$. The peak was shifted to a lower wave numbers than that observed for the x = 0 film. This shift was caused by distortion of the polycrystalline silicon owing to the presence of the added Ge atoms.

It is well known that the crystallization temperature of amorphous silicon is lowered by the presence of a certain amount of Ge atoms. 5–9 Indeed, the Raman spectrum of the x = 0.27 film shows that a polycrystalline Si-Ge film was obtained after the annealing at 800 °C. However, in the cases of x = 0.03 and 0.14, the crystallization did not progress.

The above results indicate that the crystallization of a-Si was hindered by adding a small amount of Ge atoms to the amorphous silicon deposited by the EB vapor deposition source. As a result, the temperature range in which the amorphous state was maintained and was expected to become higher. In other words, the stability of the amorphous state was expected to increase. Such a stabilization of the amorphous Si$_{0.97}$Ge$_{0.03}$ film makes it very useful as a material for electronic devices, because its electronic properties would also stabilize and be maintained over a long period of time.

B. Change in amorphous structure with annealing

To investigate the effect of annealing on the change in the amorphous structure, the Raman spectra of as-deposited films and those annealed at 600 °C and 800 °C were compared.

Figures 2(a) and 2(b) show the Raman spectra of the a-Si film with x = 0 and difference spectra, ΔI, between the individual annealing stages. The broadened bands between 200 and 500 cm$^{-1}$ originating from TO, LO, and LA phonons in the amorphous structure were observed before annealing. The ΔI obtained by subtracting the spectrum of the as-deposited film from that measured after annealing at 600 °C shows that the intensity of those broadened bands decreased after the annealing. The decrease of the TO phonon band at about 470 cm$^{-1}$ was particularly remarkable. The ΔI obtained by subtracting the spectrum measured after annealing at 600 °C from that at 800 °C showed the appearance of a sharp peak at 510 cm$^{-1}$ with a slope that stretched to 450 cm$^{-1}$. This slope is considered to be a band resulting from amorphous states in the grain boundaries of polycrystalline silicon with amorphous regions.

The decrease of the TO, LO, and LA phonon peaks likely indicates that the amorphous structure was relaxed and changed to a precursor state before its crystallization. Beeman et al.18 reported that the width of the TO phonon peak is related to the distortion of the Si bond angle. A
decrease in the amount of these phonons originating from the amorphous structure before the crystallization is associated with a rearrangement of bond angles that cause the bonds in the continuous random network to become more stable. The annealing of the pure silicon at 600 °C formed stronger and more stable bonds locally in the amorphous structure before crystallization at \( T_a = 800 \) °C. The state is considered to be a precursor state before crystallization.

Figures 3(a) and 3(b) show the Raman spectra and \( \Delta I \) for \( x = 0.14 \). The influence of the additional Ge atoms on the crystallization process is shown by the change in the Raman spectra after annealing. The broadened bands from 200 to 500 cm\(^{-1} \) assigned to TO, LO, and TA phonons increased in intensity after the annealing at 600 °C, and then decreased in intensity after annealing at 800 °C. This increase and decrease indicate changes in the amorphous state, namely, alteration of the bond angle and bond distance.

In the case of the pure silicon, a decrease in the amount of TO, LO, and LA phonons was observed after the annealing at 600 °C. However, in the Si\(_{1-x}\)Ge\(_x\) film with \( x = 0.14 \), a decrease was only observed after the annealing at 800 °C, as shown in Fig. 3. This shift to a higher temperature was attributed to the addition of Ge atoms.

To clarify the difference between these amorphous structures, the Raman spectra of the Si\(_{1-x}\)Ge\(_x\) films with \( x = 0 \) and 0.14 are compared in Fig. 4(a). The \( \Delta I \) obtained by subtracting the spectrum of the \( x = 0 \) film annealed at 800 °C from that of the \( x = 0.14 \) film annealed at 800 °C indicated that the amorphous states of both films can be considered identical. Thus, these two amorphous states may be expected to have similar distributions of bond angle and bond distance. Because the amorphous state of the \( x = 0 \) film at \( T_a = 600 \) °C is considered to be a precursor state, that of \( x = 0.14 \) at \( T_a = 800 \) °C is also considered to be a precursor state. This higher transition temperature required to transform amorphous Si\(_{1-x}\)Ge\(_x\) film with \( x = 0.14 \) to the precursor state is attributed to the addition of Ge atoms. Crystallization would occur above 900 °C, because beyond this temperature crystal grain growth progresses even in polycrystalline Si owing to bonds breaking and the re-bonding.13–16

Figure 4 also shows the \( \Delta I \) obtained by subtracting the spectrum of the as-deposited film with \( x = 0 \) from that with

![Fig. 2. Raman spectra of Si\(_{1-x}\)Ge\(_x\) film with \( x = 0 \). (a) Spectra of as-deposited film and after annealing at \( T_a = 600 \) °C and 800 °C. (b) Difference spectra, \( \Delta I \), between individual annealing stages.](image1)

![Fig. 3. Raman spectra of Si\(_{1-x}\)Ge\(_x\) film with \( x = 0.14 \). (a) Spectra of as-deposited film and after annealing at \( T_a = 600 \) °C and 800 °C. (b) Difference spectra, \( \Delta I \), between individual annealing stages.](image2)

![Fig. 4. Raman spectra of Si\(_{1-x}\)Ge\(_x\) film for \( x = 0, 0.14 \). Difference spectra, \( \Delta I \), between as-deposited Si\(_{1-x}\)Ge\(_x\) films with \( x = 0 \) and 0.14, and between films annealed at 800 °C.](image3)
x = 0.14. The broadened band at 470 cm\(^{-1}\) assigned to the TO phonon in the x = 0.14 amorphous structure was weaker than that observed for x = 0. Masuda et al.\(^{25}\) reported the appearance of TO, LO, and LA phonons with the formation of a three-dimensional amorphous silicon network during the pyrolysis of polydiarylsilane. Because the TO phonon intensity for x = 0.14 was weaker than that for x = 0, it is estimated that the x = 0.14 amorphous state had a greater bond angle and bond distance dispersion than those of the x = 0 amorphous state. The amount of TO, LO, and LA phonons increased after the x = 0.14 film was annealed at 600 °C, as shown in Fig. 3(b). Therefore, the amorphous state of the x = 0.14 film transformed into a state having a three-dimensional amorphous silicon network, similar to that of the as-deposited x = 0 film, after the annealing at 600 °C. Annealing at 800 °C was then required to transform the x = 0.14 film to the precursor state.

Although crystallization occurred at \(T_a = 800 \degree C\) in the case of x = 0, the film with x = 0.14 did not crystallize even after annealing at 800 °C. Thus, the x = 0.14 amorphous state had a higher activation energy for crystallization compared with that of x = 0. This higher activation energy is considered to have been caused by the existence of Ge atoms in the amorphous network. Yonenaga et al.\(^{23}\) reported that Si–Ge bond is longer than the Si–Si bond. If the amorphous structure is formed by a random network of quasi-tetrahedral (Q-TH) units, two types of Q-TH units existed in the amorphous film for x \(\neq 0\), one that included Ge atoms (Q-THg) and one composed of Si atoms only (Q-THs).

Because the precursor state contains local stable bonds, some rearrangement, which includes bond breaking and re-bonding, is needed to form a structure with long-range order. Such a rearrangement will be hindered by the existence of Q-THg units, because their different unit sizes stabilize the strained Q-THs units. The existence of two types of units having different sizes thereby increases the activation energy for crystallization.

Figures 5(a) and 5(b) show the Raman spectra and \(\Delta I\) spectra for x = 0.27. The crystalline silicon peak at 510 cm\(^{-1}\) was observed after the annealing at 800 °C, indicating that crystallization occurred similarly to the case of the pure amorphous silicon shown in Fig. 2. The wavenumber of the polycrystalline silicon peak was lower than that obtained for x = 0. This shift was caused by the influence of the Ge atoms.\(^{17,24,25}\) The broadened bands at 200–500 cm\(^{-1}\) assigned to the phonon bands of the amorphous structure decreased in intensity after the annealing, as shown in the \(\Delta I\) spectrum. Because a similar decrease was also observed for the a-Si with x = 0, as shown in Fig. 2(b), the precursor state existed in the x = 0.27 before crystallization. This result means that a higher concentration of Ge atoms did not stabilize the amorphous state of the Si\(_{1-x}\)-Ge\(_x\) \((x = 0.27)\) films.

Two types of units, Q-THs and Q-THg, were present in amorphous Si\(_{1-x}\)-Ge\(_x\) film when x \(\neq 0\). If the Ge atoms were distributed uniformly, both Q-THs and Q-THg units existed in the film with x = 0.14. Conversely, in the amorphous Si\(_{1-x}\)-Ge\(_x\) film with x = 0.27, all units included one Ge atom, namely, all units were Q-THg units on average. Therefore, we estimate that the coexistence of both types of quasi-tetrahedral unit, which have different unit sizes, hindered the change to the precursor state and subsequent transition to a crystalline phase, stabilizing the amorphous structure. Therefore, the proportion of Ge atoms required to stabilize the amorphous state of a-Si is considered to be less than 25%.

Roh et al.\(^6\) reported that in the case of solid phase epitaxy on the Si crystal substrate, the incubation time between the time at which the annealing was started and the time at which peaks appeared in the XRD pattern was increased by the addition of Ge atoms until x = 0.05, and then decreased with Ge concentration. Thus, the amorphous structure was likely stabilized by the addition of Ge atoms for x < 0.05 in their experiment. The differences in crystallization temperature and optimum Ge concentration between the work of Roh et al., which involved plasma-enhanced chemical vapor deposition of thin film on the crystal Si substrates, and the present study are considered to be caused by the differences in the deposition method, deposition conditions, and substrate. These parameters affect the density of dangling bonds, hydrogen concentration, impurities, and strain.

Based on the above discussion, we summarize the changes in the amorphous states as a diagram in Fig. 6. In the as-deposited films, a three-dimensional amorphous silicon network composed of quasi-tetrahedral units is formed. The amorphous state of the as-deposited Si\(_{1-x}\)-Ge\(_x\) film with x = 0.14 (indicated by \(A'\)) is different from that of the film with x = 0 (A). The \(A'\)-state has a greater bond angle and bond distance dispersion compared with that of the A-state.
After annealing at 600 °C, the Si1₋ₓGeₓ film with \( x = 0 \) changes to the precursor state (B). The Si1₋ₓGeₓ film with \( x = 0.14 \) changes to the amorphous state (B') only after annealing at 800 °C. The Raman spectra show that this B'-state is similar to the B precursor state; therefore, the B'-state is also a precursor state.

The precursor state of the \( x = 0 \) film transforms to the crystalline phase (C) after annealing at 800 °C. However, the Si1₋ₓGeₓ film with \( x = 0.14 \) requires annealing at a higher temperature to crystallize it. Because the \( x = 0.14 \) film has a larger activation energy (E') for crystallization compared with that (E) of the film with \( x = 0 \), the temperature range within which the amorphous state is maintained is widened towards a higher temperature.

During the annealing of amorphous films, the bond angle and bond distance are rearranged to a more stable state via bond breaking and re-bonding. The diamond structure of the IV group elements is constructed by the formation of sp\(^3\) hybrid orbital. Therefore, change of the amorphous state and crystallization from the amorphous state both require rearrangement of these directional bonds and therefore a large activation energy. In the case of a-Si containing Ge atoms, the Ge atoms cause distortion of the quasi-tetrahedral unit, because the bond length of the Si-Ge bond is greater than that of the Si-Si bond. The resulting Q-THg units obstruct the rearrangement of the directional bonds of the Q-THs, which consequently stabilize the amorphous state.

To clarify the crystal growth mechanism based on Q-THs and Q-THg discussed above, it is very important to investigate the effects of additional elements during nucleation and growth of a-Si on the atomic scale. We believe that \textit{in situ} observation using dynamic transmission electron microscopy would be very useful to determine the location of the nucleus and in elucidating the growth mechanism. \(^{26,27}\)

**IV. SUMMARY**

The stabilization of the amorphous structure of silicon film by adding of Ge atoms was studied using Raman spectroscopy.

The a-Si thin films containing a suitable quantity of Ge atoms required a higher temperature for crystallization than that needed to crystallize pure a-Si. Correspondingly, the temperature range in which the amorphous state was maintained became higher, and the crystallization required higher activation energy. Thus, the amorphous structure was stabilized by the addition of Ge atoms.

The Raman spectra of the as-deposited and annealed films confirmed the existence of a precursor state before the crystallization. The amount of TO, LO, and TA mode phonons, which are associated with the amorphous state, was decreased in the precursor state. The temperature at which the amorphous state changed into the precursor state also became higher than that of the pure a-Si when Ge atoms were added.

The amorphous state of as-deposited films containing Ge atoms was found to be more dispersive than that of pure a-Si. Q-THg and Q-THs units coexisted in a-Si films containing less than 25% Ge atoms. The distorted Q-THs in the amorphous state were stabilized by the existence of Q-THg, because the Si-Ge bond is longer than the Si-Si bond. This distortion of the Q-THs in the amorphous state obstructed the rearrangement of the directional bonds and prevented further changes in bond angle and bond distance, thereby stabilizing the amorphous structure.

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