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Effects of elastic stress introduced by a silicon nitride cap on solid-phase crystallization of amorphous silicon

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Effects of stress on solid-phase crystallization of amorphous silicon (*a*-Si) were studied by laser Raman spectroscopy. Compressive stress was introduced in *a*-Si with a Si₃N₄ cap. The speed of crystallization decreased with the increase of the stress while it increased again with an additional cap of SiO₂ on a Si₃N₄ cap. A SiO₂ cap introduced tensile stress in an *a*-Si film and relaxed compressive stress by a Si₃N₄ cap. The reason why crystallization of *a*-Si is suppressed is that the stress is elastic and that it does not relax with crystallization. © 1999 American Institute of Physics. [S0021-8979(99)07014-0]

I. INTRODUCTION

Polycrystalline silicon (poly-Si) is an important material in very large-scale integrated circuits (VLSI) and in an application to liquid crystal displays with driving circuits. Solid-phase crystallization of amorphous silicon (*a*-Si) is one of the methods to form a poly-Si film. It is very important, therefore, to make clear the mechanism of crystallization from *a*-Si to poly-Si in order to control properties of a poly-Si film such as a grain size, electric resistance, and thermal conductivity. However, the mechanism of crystallization of *a*-Si has not been understood clearly yet, especially since the effect of stress on crystallization of an *a*-Si film was not known at all. Very large stress is introduced in a poly-Si film on a glass substrate that is used in liquid crystal displays due to the difference of the thermal expansion coefficient between Si and glass. It has been reported that crystallization of *a*-Si started at the interface between an *a*-Si film and a substrate and that one of the driving forces of the crystallization is stress due to the difference of a thermal expansion coefficient between *a*-Si and a glass used as a substrate.¹ On the other hand, there have been reports that nucleation started at the surface of an *a*-Si film when it was kept clean.^{2,3} We also have reported that crystallization started at the surface of *a*-Si film and that larger stress was accumulated at the interface between *a*-Si and a fused silica substrate than at the surface.⁴ Laser Raman spectroscopy is one of the best methods to characterize crystallinity of a material because the phonon frequency measured by it is sensitive to the properties of the material such as the state or structure; that is amorphous or crystalline. In this study, crystallization of an *a*-Si film with stress controlled by the thickness of a silicon nitride (Si₃N₄) cap or that of a silicon dioxide (SiO₂) cap

was characterized by laser Raman spectroscopy in order to make clear the effect of stress on crystallization of an *a*-Si film.

II. EXPERIMENT

Stress cannot be estimated from the extra shift of a Raman frequency from poly-Si because the extra shift depends not only on stress but also on the grain size and the crystalline fraction. Therefore, stress introduced into poly-Si by a dielectric cap is assumed to be one accumulated in a single-crystal Si(100) on which a dielectric film is directly deposited by the rf sputtering method. It was characterized by laser Raman spectroscopy based on the extra shift of a Raman frequency.

The sample used for study of crystallization had a structure SiO₂/Si₃N₄/*a*-Si/Si₃N₄/Si(100) and Si₃N₄/*a*-Si/Si₃N₄/Si(100). Dielectric films, such as Si₃N₄ and SiO₂ and an *a*-Si film were deposited by the rf sputtering method at room temperature on a Si(100) substrate. The thickness of a Si₃N₄ film on Si(100) and that of an *a*-Si film were 50 nm and 1.5 μm, respectively. For the samples without a SiO₂ cap, the thickness of a Si₃N₄ cap was varied from 50 to 1000 nm and for those with a SiO₂ cap, the thickness of a Si₃N₄ cap was fixed at 750 nm and that of a SiO₂ cap was varied from 200 to 600 nm. All samples were annealed at 500 °C for 6 h in Ar+H₂ (6%) in order to stabilize films and were annealed at 750 °C in the same atmosphere in order to transform *a*-Si into poly-Si. Dielectric caps on an *a*-Si film were removed after all annealing.

The crystallinity was characterized also by laser Raman spectroscopy. Raman spectra were obtained using a triple-monochromator JEOL JRS-400T. The wavelength of the probe light was 514.5 nm. A Si₃N₄ cap and a SiO₂ cap were removed before the measurement of laser Raman spectroscopy because a Raman peak of *a*-Si is so weak and broad that it cannot be measured without removing a Si₃N₄ cap which absorbs the probe light.

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FIG. 1. Definition of the crystalline fraction χ . A typical Raman spectrum of p -Si consists of two peaks: one due to the crystal and the other due to a -Si. A crystalline fraction χ is defined by $I_p/(I_p + \gamma I_a)$, where I_p and I_a are the area of the peak due to crystal and a -Si, respectively, and γ is the ratio of the scattering cross section.

As shown in Fig. 1, the crystalline fraction χ of poly-Si was obtained from a Raman spectrum using the expression,

$$\chi = \frac{I_p}{I_p + \gamma I_a}, \quad (1)$$

where I_p and I_a are the areas of the peaks of poly-Si and a -Si, respectively, and γ is the ratio of the scattering cross section. γ is a very important factor to estimate the crystalline fraction from a Raman spectrum but it varies with grain size. It has been reported that the value of γ is 0.88 when a grain size is small or when crystalline fraction is small.⁵ In this study the early stage of crystallization is discussed. Therefore, 0.88 was used as the value of γ . I_p and I_a were obtained by means of the least squares method assuming that the shape of a poly-Si peak was Lorentzian and that of an a -Si peak was Gaussian.

III. RESULTS AND DISCUSSION

Figure 2 shows Raman shift for a Si(100) substrate in which stress was accumulated by a Si_3N_4 film or a SiO_2 film at a room temperature. Raman shift of the reference which was a stress-free Si(100) substrate without dielectric films

FIG. 2. Raman shift of a Si(100) substrate stressed by a Si_3N_4 film or a SiO_2 film.

FIG. 3. Dependence of the Raman spectrum from a poly-Si film with a Si_3N_4 cap on the thickness of a Si_3N_4 cap.

was 520.5 cm^{-1} . Raman shift for a Si(100) substrate with a Si_3N_4 cap was larger than that for the reference and increased with the thickness of a Si_3N_4 cap. A Si_3N_4 cap annealed at 500°C introduced compressive stress into the Si(100) substrate at room temperature and the quantity of the stress was independent of annealing at 750°C following annealing at 500°C . When the thickness of a Si_3N_4 cap was $1 \mu\text{m}$, stress in a Si(100) substrate estimated from an extra peak shift was $1.17 \times 10^9 \text{ dyn/cm}^2$, which was 2 orders larger than that estimated by the bimetal model assuming that the stress was caused by a difference of the thermal expansion coefficients between a Si_3N_4 cap and a Si substrate. The compressive stress by a Si_3N_4 cap was independent of temperature because it was not due to the difference of the thermal expansion coefficient, but was due to the intrinsic stress in a Si_3N_4 cap.⁶

Raman shift for a Si(100) substrate with a $\text{SiO}_2/\text{Si}_3\text{N}_4$ (750 nm) cap decreased with the thickness of a SiO_2 cap. A SiO_2 cap relaxed stress introduced by a Si_3N_4 cap because the nature of stress by a SiO_2 cap is opposite to that by a Si_3N_4 cap, that is, stress by a SiO_2 cap is tensile and that by a Si_3N_4 cap is compressive.

Figure 3 shows the Raman spectra from a -Si films with only a Si_3N_4 cap. The samples were annealed at 750°C for 5 min after annealing at 500°C for 6 h. The spectrum consists of two peak. One was around 520 cm^{-1} corresponding to crystalline Si(c -Si). The other was a broad peak around 480 cm^{-1} corresponding to a -Si. Obviously, the intensity of the Raman peak from c -Si decreased with the thickness of a Si_3N_4 cap. Figure 4 shows the crystalline fraction versus annealing time which was obtained from Raman spectra. An a -Si film with a thin Si_3N_4 cap crystallized faster than that with a thick Si_3N_4 cap. A value of crystalline fraction saturated finally to almost the same one for all samples and the value did not depend on the thickness of the Si_3N_4 cap, although the absolute value contained some errors because the value of scattering cross section depends on the grain size of poly-Si.

FIG. 4. The crystalline fraction of poly-Si vs annealing time.

Figure 5 shows Raman spectra from the samples with a SiO_2 cap which was deposited on a Si_3N_4 cap of 750 nm. An intensity of Raman peak from poly-Si increased with the thickness of a SiO_2 cap and the speed of crystallization suppressed by a Si_3N_4 film was recovered again. When it was assumed that the suppression of the crystallization by a Si_3N_4 cap would be due to sputtering, the effect of a SiO_2 cap must be the same as that of a Si_3N_4 cap. However, the effect of a SiO_2 cap on a Si_3N_4 cap was opposite to that of a

FIG. 5. Dependence of the Raman spectrum from a poly-Si film with a $\text{SiO}_2/\text{Si}_3\text{N}_4(750\text{ nm})$ cap on the thickness of a SiO_2 cap.

Si_3N_4 cap. Therefore, the suppression of crystallization by a Si_3N_4 cap was due to compressive stress introduced into an a -Si film.

We need to distinguish between elastic and plastic strain in discussing effects of strain on crystallization. Strain in this work is elastic while strain which has been considered to promote crystallization is plastic. We propose in this paper that elastic strain, which is introduced in this work, does not relax with phase transformation while plastic strain relaxes with phase transformation and promotes crystallization. Elastic modulus of c -Si is larger than that of a -Si.^{7,8} Therefore, elastic strain which does not relax causes an increase of strain energy with phase transformation, assuming that strain shows no change with phase transformation when crystalline fraction is small. Consequently the difference of free energy between a -Si and c -Si decreases with strain in an a -Si film. As a result, crystallization was suppressed.

IV. CONCLUSION

Effects of stress on solid-phase crystallization in an a -Si film was studied by laser Raman spectroscopy. We found that compressive stress suppresses the speed of crystallization which can be controlled by a simple method in which compressive stress is adjusted by controlling a thickness of a Si_3N_4 cap or SiO_2 cap on an a -Si film. A Si_3N_4 cap introduced compressive stress and a SiO_2 cap introduced tensile stress. That is, a Si_3N_4 cap on an a -Si film suppresses crystallization while another SiO_2 cap on a Si_3N_4 cap recovers the speed of crystallization suppressed by a Si_3N_4 cap. The reason why stress suppresses crystallization of an a -Si film is that introduced strain is elastic and that it does not relax with crystallization. Elastic strain that does not relax causes an increase in strain energy with phase transformation because elastic modulus of c -Si is larger than that of a -Si^{7,8} and the difference of free energy between a -Si and c -Si decreases. As a result, elastic stress suppresses crystallization.

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