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Pulsed Laser-Induced Amorphization of Polycrystalline Silicon Film

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A 20 nm-thick polycrystalline silicon film was completely amorphized through laser-induced melt-regrowth using a 30 ns XeCl excimer laser pulse at an energy density of over 240 mJ/cm^2. Moreover, the amorphized silicon was recrystallized by irradiation by a single pulse at an energy density below 240 mJ/cm^2. The transition from the amorphous to the crystalline state was reversible and governed by the laser energy density. The laser-induced amorphized film had a low optical band gap of 1.4 eV. Its electrical conductivity was characterized by variable-range hopping.

KEYWORDS: laser-induced amorphization, laser-induced crystallization

§1. Introduction

Pulsed laser-induced melt-regrowth has been studied by many researchers to clarify phenomena such as crystallizing amorphous silicon and amorphizing crystalline silicon.[1-8] Thompson *et al.*[8] reported that a near-surface region of a silicon-on-sapphire (SOS) film was amorphized by rapid quenching of molten silicon with a regrowth velocity greater than 15 m/s with irradiation from a 2.5 ns pulsed laser at near melting threshold energy. However, complete amorphization of the silicon film was not demonstrated because molten silicon recrystallized with irradiation for energy densities much larger than the melting threshold energy. If a silicon film can be completely amorphized, laser-induced amorphization will be an attractive technique for preamorphization in solid-state grain growth[9] and for optical switching memory application.[10]

This paper is the first report of the complete amorphization of a thin polycrystalline silicon (poly-Si) film using a pulsed XeCl excimer laser. Analysis of the reversible transition from the amorphous to the crystalline state is also discussed.

§2. Experimental

20 nm- and 40 nm-thick a-Si:H and 20 nm-thick phosphorus-doped hydrogenated amorphous silicon (a-Si:H,P) films were deposited on a quartz substrate at 250°C using radio-frequency glow discharge (rf-GD). 50SCCM SiH_4 gas diluted to 10% with Ar (SiH_4(10%)/Ar) mixed with 50SCCM H_2 gas was decomposed for depositing a-Si:H. 50SCCM SiH_4(10%)/Ar and 10SCCM PH_3(1%)/Ar mixed with 50SCCM H_2 gas was also decomposed for depositing a-Si:H,P. The samples were then placed into a vacuum chamber and the chamber was evacuated to 10^{-5} Torr. XeCl-308 nm excimer laser pulses (30 ns-FWHM) were then irradiated normal to the sample surface through a quartz window. The laser beam was formed into a 5 mm × 10 mm rectangle through a lens at the sample surface. The melting threshold energy of a-Si:H was 130 mJ/cm^2, which was determined using time-resolved optical reflectivity and transient conductance measurements.[11]

Since the a-Si:H film contained 10 atomic percent of hydrogen atoms, the sample was crystallized by irradiation with 5 pulses whose energy density was increased from 140 to 220 mJ/cm^2; this multistep irradiation prevented eruption of hydrogen atoms which can cause surface roughness. After crystallization, the samples were irradiated with the pulses at an energy density between 220 and 280 mJ/cm^2. After the irradiation, the samples still had a smooth surface; the roughness was ±1.5 nm. Properties of the films were investigated by measuring optical reflectivity and transmissivity, Raman scattering and electrical conductivity.

§3. Results and Discussion

The a-Si:H film was crystallized through a rapid melt-regrowth process. The maximum duration of melt was 100 ns during the multistep irradiation, as obtained by transient conductance measureemts.[11] Transmission electron micrography (TEM) observation revealed that the grain size was between 5 and 30 nm. The poly-Si film had a hydrogen concentration lower than 0.2 atomic percent, which was obtained by the Fourier transform spectroscopy (FTIR) measurements of the absorption of the stretching vibration mode of the silicon-hydrogen bonding.

The 20 nm-thick as-deposited a-Si:H film did not show the peak in optical reflectivity around 275 nm (E_2 peak) caused by a transition at point X in the Brillouin zone of crystalline silicon,[12] as shown by curve A in Fig. 1. Moreover, it showed a Raman scattering spectrum with a broad TO phonon Stokes peak around 500 cm^{-1} and a tail on the low-frequency side, which were assigned to the amorphous mode by Iqbal and Veprek,[11] as shown by curve A in Fig. 2. When the 20 nm-thick poly-Si film was irradiated with pulses at an energy density greater than 240 mJ/cm^2, the film showed almost the same optical reflectivity and Raman scattering spectra as the as-deposited a-Si:H film, as shown by curve C in Fig. 1 and Fig. 2. These results show that the poly-Si film was amorphized by irradiation with a pulse at an energy density greater than 240 mJ/cm^2 Laser-induced amorphization was caused by multipulse irradiation as well as single pulse irradiation. This means that the transitions from

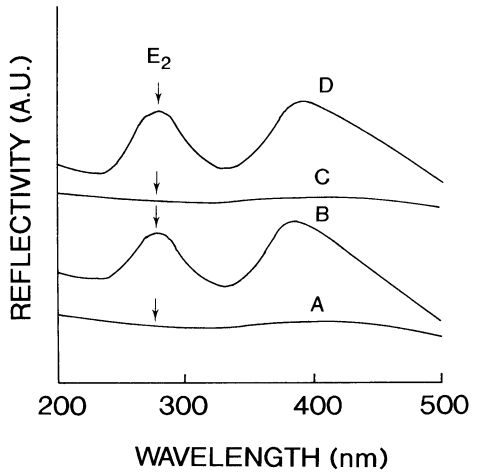

Fig. 1. Optical reflectivity spectra for as-deposited 20 nm-thick a-Si:H film (A), poly-Si film fabricated by the multistep irradiation (B), irradiated with a single pulse at 260 mJ/cm^2 after the crystallization (C) and irradiated with two pulses at 260 mJ/cm^2 followed by 220 mJ/cm^2 after the crystallization (D). The arrows show the E_2 peak.

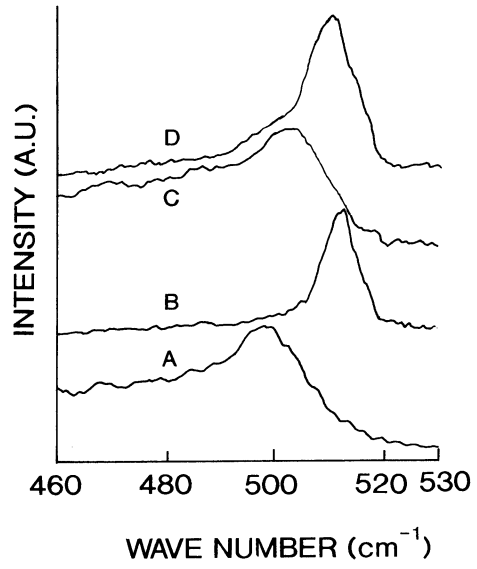

Fig. 2. Raman scattering spectra for as-deposited 20 nm-thick a-Si:H film (A), poly-Si film fabricated by the multistep irradiation (B), irradiated with a single pulse at 260 mJ/cm^2 after the crystallization (C) and irradiated with two pulses at 260 mJ/cm^2 followed by 220 mJ/cm^2 after the crystallization (D).

amorphous to melt to amorphous also occurred in the thin film, caused by irradiation at an energy density greater than 240 mJ/cm^2. The threshold energy density for amorphization increased from 240 to 250 mJ/cm^2 as the thickness of film was increased from 20 to 40 nm.

It was also found that the laser-induced amorphized silicon film was recrystallized by irradiation with a pulse at an energy density below 240 mJ/cm^2. The E_2 peak appeared in the optical reflectivity spectrum as shown by curve D in Fig. 1. The TO phonon Stokes peak associated with polycrystalline silicon exhibited a sharper peak around 510 cm^{-1} [13] in the Raman scattering spectrum, as shown by curve D in Fig. 2. These spectra was quite similar to those of the poly-Si film, as is shown by the curves B in Figs. 1 and 2.

The Raman spectra for the amorphous silicon films show no evidence of a crystalline state and the Raman spectra for the poly-Si films show no evidence of an amorphous state, as can be seen in Fig. 2. This means that the silicon film was completely transited to amorphous or crystalline states through the laser-induced melt-regrowth.

The optical absorption coefficients were obtained from the optical reflectivity and transmissivity spectra. The 20 nm-thick laser-induced amorphized silicon film had a larger optical absorption coefficient for photon energy between 1.5 eV and 3.0 eV than the as-deposited a-Si:H film, as is shown in Fig. 3 by curves C and A, respectively. The optical band gap obtained by the Tauc plot [14] ($(\alpha \cdot \hbar\omega \cdot n)^{0.5}$ vs $\hbar\omega$) was 1.4 eV for the laser-induced amorphized film and 1.8 eV for the as-deposited a-Si:H film, respectively. The large optical absorption coefficient and the small optical band gap indicate that the laser-induced amorphized film has the large density of gap states associated with dangling bonds, as is observed in nonhydrogenated amorphous silicon fabricated by evaporation and sputtering.

Laser-induced amorphization and recrystallization were also observed in the phosphorus-doped (P-doped) poly-Si film. Figure 4 shows the temperature dependence of conductivity for the nondoped and P-doped silicon films. The conductivity for the nondoped initial poly-Si film and the recrystallized film after amorphization increased by an activation energy of 0.45 eV with increasing temperature from 180 K, as shown by curves a and c in Fig. 4, respectively. The P-doped initial poly-Si film and recrystallized film after amorphization have large conductivity of 1000 and 930 S/cm, respectively. Their conductivity did not change with temperature between 100 K and 350 K, as shown by curves d and f in Fig. 4. This result is interpreted by the formation of an impurity band through laser-induced melt-regrowth, because both the P-doped poly-Si films had a large carrier concentration of 1.2×10^{21} cm^{-3}, as obtained by the Hall effect measurement.

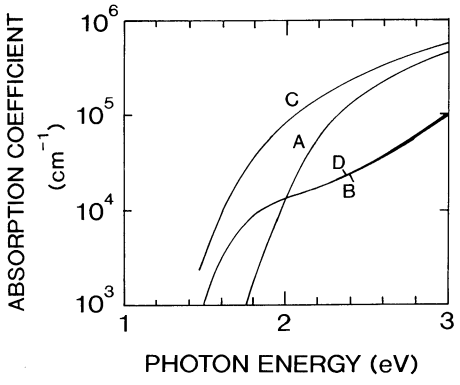

Fig. 3. Optical absorption coefficient as a function of photon energy for as-deposited 20 nm-thick a-Si:H film (A), poly-Si film (B), amorphized film by irradiation with a single pulse at 260 mJ/cm^2 (C) and recrystallized film by irradiation with a pulse at 220 mJ/cm^2 following amorphization (D).

On the other hand, the conductivity for nondoped and P-doped laser-induced amorphized films did change with temperature, but the change was less than that for the nondoped poly-Si films and the conductivity was quite insensitive to phosphorus doping, as shown by curves b (nondoped) and e (P-doped) in Fig. 4. The logarithm of the conductivity for laser-induced amorphized films is nearly proportional to $(1/T)^{1/4}$ for temperatures between 100 and 230 K, as shown in Fig. 5. The temperature dependence of the conductivity, therefore, can be assumed to be caused by variable-range hopping.[15] The conductivity was fitted to the formula $\sigma=\sigma_0 \exp(-T_0/T)^{1/4})$. From Fig. 5, σ_0 and T_0 were 7×10^4 s/cm and 2.8×10^7 K for the nondoped amorphous film and 1×10^5 S/cm and 1.4×10^7 K for the P-doped amorphous film. If the spatial decay constant of a localized wave function is 0.2 Å^{-1},[16] the density of localized states at the Fermi level, the hopping distance and the hopping energy were obtained using the experimental data of T_0. They were 5.3×10^{19} cm$^{-3}\cdot$eV^{-1}, 44 Å and 0.05 eV for the nondoped amorphous silicon, and 1.06×10^{20} cm$^{-3}\cdot$eV^{-1}, 37 Å and 0.04 eV for the P-doped amorphous silicon, respectively.

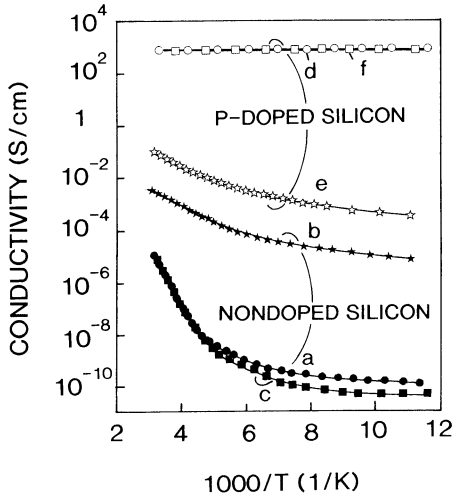

Fig. 4. Conductivity as a function of temperature. (a), (b) and (c) represent 20 nm-thick nondoped silicon: poly-Si (a), amorphized film by irradiation with a pulse at 260 mJ/cm^2 (b) and recrystallized film by irradiation with a pulse at 220 mJ/cm^2 following amorphization (c). (d), (e) and (f) represent 20 nm-thick phosphorus-doped silicon: poly-Si film (d), amorphized film by irradiation with a pulse at 260 mJ/cm^2 (e) and recrystallized film by irradiation with a pulse at 220 mJ/cm^2 (f) following amorphization.

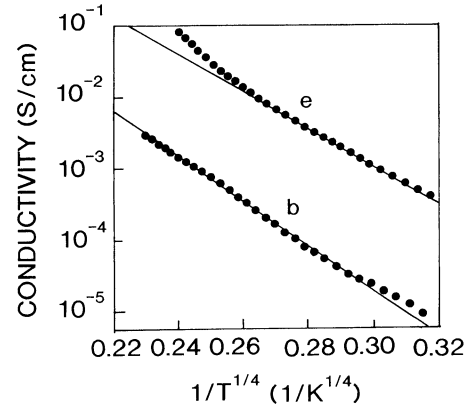

Fig. 5. Conductivity as a function of temperature $(1/T^{1/4})$ for 20 nm-thick nondoped amorphized film (b) and P-doped amorphized film (e).

We found that the 20 nm-thick silicon film was amorphized completely by irradiation for an energy density greater than 240 mJ/cm^2 as described above. Complete amorphization indicates that silicon was melted throughout the film by irradiation for an energy density above the threshold. Thompson *et al.* have pointed out that amorphization of supercooled molten silicon occurs when the regrowth velocity exceeds 15 m/s,[8] so we believe that rapid solidification will occur if there is supercooling in molten silicon on the quartz substrate, although this has not been proven experiemntally. We have already found that poly-Si films were melted and then crystallized at a velocity of no more than 1 m/s by irradiation at an energy density lower than 240 mJ/cm^2.[11] We deduce, therefore, there can be no supercooling of molten silicon when the silicon film is melted by irradiation at an energy density lower than 240 mJ/cm^2.

§3. Conclusions

Laser-induced amorphization was first observed in a poly-Si film. The 20 nm-thick poly-Si film was completely amorphized with a 30 ns-XeCl excimer laser pulse at an energy density greater than 240 mJ/cm^2. The threshold energy density for amorphization increased as the film thickness increased. Moreover, the amorphous film was completely recrystallized by irradiation with a pulse at an energy density of 220 mJ/cm^2. The laser-induced amorphized film had a larger optical absorption coefficient for photon energies between 1.5 and 3.0 eV than the as-deposited a-Si:H film and a small optical band gap of 1.4 eV. This suggests that the laser-induced amorphized film has the large density of gap states associated with dangling bonds. The electrical conductivity for the amorphous film was quite insensitive to phosphorus doping. The temperature dependence of the conductivity was characterized by variable range hopping. The density of localized states at the Fermi level was 5.3×10^{19} cm$^{-3}\cdot$eV^{-1} for the nondoped amorphous film and 1.06×10^{20} cm$^{-3}\cdot$eV^{-1} for the P-doped amorphous film.

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