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Crystalline Properties of Laser Crystallized Silicon Films

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The carrier mobility of phosphorus-doped laser crystallized polycrystalline silicon (poly-Si) films was investigated. An analysis of the free carrier optical absorption spectra gave the carrier mobility, 6–11 cm^2/V·s, for the laser energy between 140 (the crystallization threshold) and 280 mJ/cm^2. The mobility increased as the temperature decreased from 473 K to 77 K because of the reduced carrier scattering by the lattice vibration as in single crystalline silicon. On the other hand, the carrier mobility obtained by the Hall effect measurements increased from 1 to 5 cm^2/V·s as the laser energy increased. The mobility for samples crystallized near the crystalline threshold decreased as the temperature decreased from 473 K to 77 K. This is probably caused by lack of the thermal excitation energy for crossing the energy barrier at the grain boundary.

KEYWORDS: optical absorption spectra, free carrier absorption, Hall effect, carrier density, carrier mobility

The pulsed-laser-induced crystallization has been applied to the fabrication of thin film transistors (TFTs).[1–5] The crystallization of silicon films and the activation of dopant are realized without heating the substrates to a high temperature. They are suitable for low temperature processing, which is useful for the fabrication of the TFTs on an inexpensive glass substrate for liquid crystal display (LCD) devices. The electrical properties of laser crystallized silicon films have been analyzed using the Hall effect measurements or transistor characteristics.[6–8] These measurements give the mobility and density of the carriers which propagate between electrodes crossing many grain boundaries in the poly-crystalline silicon (poly-Si) films. The average energy barrier height at grain boundaries has been also investigated with the above methods. On the other hand, the free carrier absorption analysis provides the electrical properties, the carrier mobility and the carrier density in the crystalline grains because the free carrier absorption occurs via excitation caused by the electrical field of incident photons followed by energy relaxation in the crystalline grains.[9,10]

This paper applies the results of the free carrier optical absorption analyses as well as the Hall effect measurements to the characterization of the electrical properties of phosphorus-doped laser crystallized silicon films. Temperature changes in the mobility are reported in our discussion on crystalline properties. Dependence of the carrier mobility on the crystallization laser energy obtained by those two methods is also discussed.

Doped polycrystalline silicon films 30–35 nm thick were fabricated by XeCl excimer laser heating of 2.5%-phosphorus-doped amorphous silicon films formed by plasma enhanced chemical vapor deposition on quartz glass substrates. The threshold energy for crystallization was 140 mJ/cm^2. The multiple-step-energy irradiation was conducted to release hydrogen atoms from the films and to form poly-Si films with a smooth surface. The laser energy was increased from the threshold to 280 mJ/cm^2 with a 10 mJ/cm^2 step. Three pulses were irradiated for each laser energy step. Undoped laser crystallized silicon films were also fabricated.

The Hall effect measurements were carried out at 77 K in liquid nitrogen, at room temperature (295 K) and at 473 K for samples with a size of 5 mm×5 mm with Al electrodes formed at each corner to obtain the carrier mobility and the carrier density.

The optical free carrier absorption was measured using a conventional spectrometer (Hitachi U-3400) at 77 K, 295 K and 473 K. For low temperature measurements, a cryostat with optical transmittance windows (Oxford-Instruments Continuous Flow) was used. For high temperature measurements, the samples were placed on a heater, which was fabricated by a Cr thin film formed on a transparent quartz substrate. The Cr film was patterned to have a small window for optical measurements. Transmittance spectra of the undoped polycrystalline silicon films were first measured at wavelength from 1.1 μm to 2.5 μm to determine the refractive index of the silicon film by the analysis of the optical interference at air/Si/substrate at those temperatures. Transmittance (T)at the surface region of air/Si/substrate is given as[11]

$$T=\left|t_0t_1\exp(\mathrm{i}4\pi\tilde{n}_{\mathrm{Si}}d\lambda^{-1})\left(1+r_0r_1\exp(\mathrm{i}4\pi\tilde{n}_{\mathrm{Si}}d\lambda^{-1})\right)^{-1}\right|^2$$

$$t_0=2(1+\tilde{n}_{\mathrm{Si}})^{-1},$$

$$r_0=(1-\tilde{n}_{\mathrm{Si}})(1+\tilde{n}_{\mathrm{Si}})^{-1}$$

$$t_1=2\tilde{n}_{\mathrm{Si}}(\tilde{n}_{\mathrm{Si}}+n_{\mathrm{SiO2}})^{-1},$$

$$r_1=(\tilde{n}_{\mathrm{Si}}-n_{\mathrm{SiO2}})(\tilde{n}_{\mathrm{Si}}+n_{\mathrm{SiO2}})^{-1}$$

$$\tilde{n}_{\mathrm{Si}}=n_{\mathrm{Si}}+ik_{\mathrm{Si}} \qquad (1)$$

where d is the film thickness, λ is the wavelength, n_{SiO2} is the refractive index of the quartz substrate and $\tilde{n}_{\mathrm{Si}}$ is the complex refractive index of Si, which consists of the refractive index (n_{Si}: real part) and the extinction coefficient (k_{Si}: imaginary part). The extinction coefficient was low enough to assume that k_{Si} is zero in this wavelength range. A small reflection at the air/substrate surface, was considered for calculation of the transmittance of the samples. The refractive index spectra of the undoped silicon film were obtained by fitting calculated transmittance spectra to the experimental spectra. Then, the transmittance spectra of doped silicon were measured at those temperatures. The free carrier absorption causes change in the refractive index as well as in the extinction coefficient, as in following equations,[9]

$$n = \frac{1}{\sqrt{2}}\left[n_{\mathrm{Si}}^2 - A + \left\{(n_{\mathrm{Si}}^2 - A)^2 + \frac{A^2e^2\lambda^2}{4\pi^2m^2c^2\mu^2}\right\}^{0.5}\right]^{0.5}$$

$$k = \frac{1}{\sqrt{2}}\left[A - n_{\mathrm{Si}}^2 + \left\{(n_{\mathrm{Si}}^2 - A)^2 + \frac{A^2e^2\lambda^2}{4\pi^2m^2c^2\mu^2}\right\}^{0.5}\right]^{0.5}$$

$$A = Nm\mu^2\varepsilon_0^{-1}(1 + 4\pi^2m^2\mu^2c^2e^{-2}\lambda^{-2})^{-1} \qquad (2)$$

where n_{Si} is the refractive index of undoped silicon, which was obtained by the interference calculation with the transmittance spectra of the undoped silicon films, c is the velocity of light in vacuum, e is the electrical charge, m is the effective mass of the carrier, 4.0×10^{-31} Kg, which was determined by Miyao *et al.*[12] from the investigation of the optical properties of phosphorus doped silicon, λ is the wavelength, μ is the carrier mobility and N is the carrier density. The experimental transmittance spectra were compared to the spectra obtained by the interference calculation with the refractive index and the extinction coefficient given by the eq. (2) with changing parameters of the carrier mobility and the carrier density until best coincidence of those spectra was obtained.

The free carrier optical absorption was also measured at room temperature for samples crystallized at different energies. In this case, absorption spectra were obtained using a reflectance system with a total reflectance mirror placed on the rear side of the sample[10,13] for more precise measurements. However, the transmittance spectra were used for measuring the temperature dependence of the free carrier absorption because of a space limitation of the measurement booth of the spectrometer. The absorption coefficient, α, is given as, $\alpha = (-1)/(2d)\ln(R - r)/(1 - r)$, where d is the film thickness, r is the reflectivity at the film surface and R is the reflectivity with a total reflectance mirror. The experimental accuracy was $100\ \mathrm{cm}^{-1}$ for 40-nm-thick films. Using the relation between the optical absorption coefficient and the extinction coefficient, $\alpha = 4\pi k/\lambda$, the carrier mobility and the carrier density were obtained by the process of fitting calculated absorption spectra using eq. (2) to the experimental spectra.

Figure 1 shows the transmittance spectra measured at 77 K, room temperature (295 K) and 473 K as well as the calculated spectra best fitted with parameters of the carrier mobility and carrier density for the films crystallized at 160 mJ/cm^2 (a) and 280 mJ/cm^2 (b). In both the spectra shown in (a) and (b), the transmittance increased as the wavelength increased from 1.1 μm because of the optical interference effect. On the other hand, the free carrier absorption reduced the transmittance in the longer wavelength region because the free carrier absorption is larger for a longer wavelength as shown by the extinction coefficient in the eq. (2). The increase in transmittance was observed as the temperature decreased from 473 K to 77 K. This resulted from the increase of carrier mobility.

Table I summarizes the carrier mobility and the carrier density obtained by the analyses of free carrier optical absorption as well as the Hall effect measurements. The carrier mobility obtained by the analyses of free carrier optical absorption increased monotonically as the temperature decreased from 473 K to 77 K for the samples crystallized at 160 mJ/cm^2 and 280 mJ/cm^2. There is no appreciable change in the carrier density with tem-

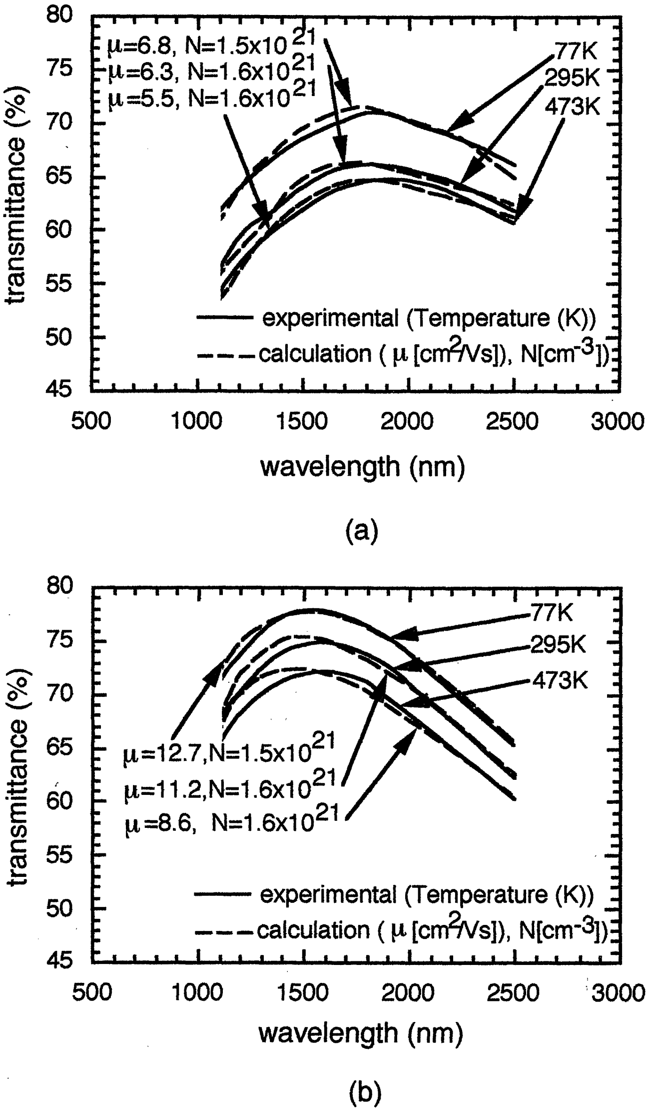

Fig. 1. Transmittance spectra measured at 473 K, 295 K and 77 K for 2.5% phosphorus-doped poly-Si crystallized at 160 mJ/cm^2 with a thickness of 35 nm (a) and at 280 mJ/cm^2 with a thickness of 30 nm (b). Dashed curves represent spectra calculated with the free carrier optical absorption theory best fitted with the parameters of carrier mobility (μ) and carrier density (N)given in the figure.

Table I. The carrier mobility (μ) and carrier density (N) obtained by the analyses of free carrier optical absorption measured and Hall effect measured at temperatures 473 K, 295 K and 77 K for samples crystallized at 160 mJ/cm^2 and 280 mJ/cm^2.

Laser energy	Temperature	Free carrier absorption		Hall effect	
		μ	N	μ	N
(mJ/cm^2)	(K)	(cm^2/V·s)	(cm^{-3})	(cm^2/V·s)	(cm^{-3})
160	77	6.8	1.5×10^{21}	1.1	1.0×10^{21}
	295	6.3	1.6×10^{21}	1.5	1.0×10^{21}
	473	5.5	1.6×10^{21}	1.8	1.0×10^{21}
280	77	12.7	1.5×10^{21}	5.1	1.5×10^{21}
	295	11.2	1.6×10^{21}	5.2	1.4×10^{21}
	473	8.6	1.6×10^{21}	4.8	1.4×10^{21}

perature change. The mobility increase is interpreted as reduced carrier scattering caused by the lattice vibration. On the other hand, the Hall effect measurements revealed that the mobility slightly decreased as the temperature decreased from 473 K to 77 K for the sample crystallized at 160 mJ/cm^2, while the poly-Si film formed at 280 mJ/cm^2 had almost the same mobility at those temperatures. Although the free carrier absorption can be caused by carriers inside crystalline grains, the electrical current must traverse many grain boundaries, so it strongly depends on grain boundary properties. If the grain boundary properties are poor and the average energy barrier at the boundaries is high, the carrier mobility obtained from the Hall effect current decreases as the temperature decreases because the thermal excitation energy for crossing the boundaries is reduced. The average energy barrier height (ΔE) was roughly estimated by simply assuming the mobility obtained by the Hall effect measurements (μ_H) as, $\mu_H = \mu_A \exp(-\Delta E/(kT))$, where μ_A is the mobility obtained by the free carrier optical absorption, k is the Boltzmann constant and T is the absolute temperature. From the results at 77 K–473 K, the average energy barrier height was 12–45 meV for the sample crystallized at 160 mJ/cm^2, and 6–24 meV for the sample crystallized at 280 mJ/cm^2. The energy barrier height was reduced by the high crystallization energy.

Figure 2 shows the carrier mobility obtained from analyses of the free carrier optical absorption and Hall effect measurements as functions of the crystallization laser energy. The free carrier optical absorption analysis provided the carrier mobility which gradually increased from 6 to 10 cm^2/V·s as the laser energy increased from 140 to 280 mJ/cm^2. The result indicates that crystalline grains formed by the low laser energy (near the crystalline threshold) have a good quality, similar to that of the film formed by high laser energy. The small increase in the mobility with increasing the laser energy was probably caused by increase of the grain size. On the other hand, the carrier mobility obtained by the Hall effect measurements increased from 1 cm^2/V·s to 5 cm^2/V·s as the laser energy increased from 140 mJ/cm^2 to 280 mJ/cm^2. The increase of the carrier mobility obtained by the Hall effect measurements with the increasing laser energy is interpreted as the improvement of the grain boundary properties with laser irradiation at a higher energy, as some researchers have reported.$^{14)}$The disordering at the grain boundary would be reduced by the high energy irradiation because of the long melt duration and the low quenching rate.$^{15)}$ The dangling bond density is reduced by the long melt duration caused by the high energy irradiation.

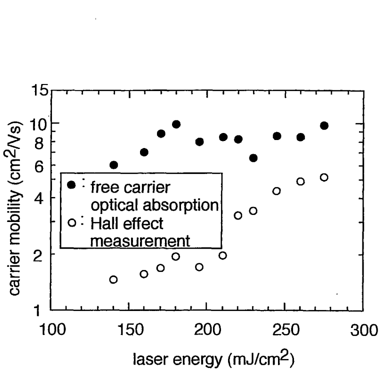

Fig. 2. The carrier mobility obtained by analyses of the free carrier optical absorption and Hall effect measurements as functions of the laser energy.

In summary, the carrier mobility of phosphorus doped laser crystallized silicon films was investigated with the analyses of the free carrier optical absorption and Hall effect measurements. The mobility obtained by the free carrier absorption increased as the temperature decreased from 473 K to 77 K for poly-Si films formed by irradiation at 160 mJ/cm^2 and 280 mJ/cm^2. This is interpreted as reduced carrier scattering caused by the lattice vibration. On the other hand, the Hall effect measurements revealed that the mobility decreased for the films crystallized at 160 mJ/cm^2, while there was almost no change in the mobility for the films crystallized at 280 mJ/cm^2. These results indicate that the laser crystallization forms good crystalline grains with a high carrier mobility. However, the grain boundary is poor for the crystallization produced at a low energy. The energy barrier height was estimated at 12∼45 meV from the mobility for the 160 mJ/cm^2-crystallization case. The analysis of free carrier absorption spectra revealed that the poly-Si film had a high carrier mobility (6∼10 cm^2/V·s) for crystallization laser energy between 140 and 280 mJ/cm^2. On the other hand, the mobility obtained by the Hall effect measurements increased from 1 to 5 cm^2/V·s as the laser energy increased from 140 and 280 mJ/cm^2. These results show that the laser irradiation at a higher energy improves grain boundary properties and reduces the energy barrier height at the grain boundary.

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