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Description	



Anisotropic electrical conduction and reduction in dangling-bond density for polycrystalline Si films prepared by catalytic chemical vapor deposition

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Polycrystalline Si (poly-Si) films with high crystalline fraction and low dangling-bond density were prepared by catalytic chemical vapor deposition (Cat-CVD), often called hot-wire CVD. Directional anisotropy in electrical conduction, probably due to structural anisotropy, was observed for Cat-CVD poly-Si films. A novel method to separately characterize both crystalline and amorphous phases in poly-Si films using anisotropic electrical conduction was proposed. On the basis of results obtained by the proposed method and electron spin resonance measurements, reduction in dangling-bond density for Cat-CVD poly-Si films was achieved using the condition to make the quality of the included amorphous phase high. The properties of Cat-CVD poly-Si films are found to be promising in solar-cell applications. © 1999 American Institute of Physics.

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I. INTRODUCTION

Polycrystalline silicon (poly-Si) is one of the promising materials for large-area thin-film electronic devices, such as solar cells and thin-film transistors (TFTs) in liquid crystal displays, with the possibility to take the place of hydrogenated amorphous silicon (*a*-Si), in which there are problems, for example, due to photodegradation, often called Staebler-Wronski effect,¹ and low carrier mobility.

Catalytic chemical vapor deposition (Cat-CVD), often called hot-wire CVD, is one of the promising low-temperature deposition techniques.² In the Cat-CVD method, deposition gases are decomposed by catalytic cracking reactions with a heated catalyzer placed near substrates. Since an increase in the substrate temperature due to heat radiation is suppressed below 300 °C, low-temperature film formation is realized without plasma excitation, bringing about no plasma damage. Large-area deposition is also possible only by enlarging the covering area of the catalyzer. These are all the advantages of Cat-CVD method in comparison with the plasma-enhanced chemical vapor deposition (PECVD) method. So far, the preparation of *a*-Si,³⁻⁶ poly-Si^{7,8} and silicon nitride (SiN_x)^{9,10} by Cat-CVD have been reported.

In the previous study, the transmission electron microscopy (TEM) observation revealed that Cat-CVD poly-Si films with high crystalline fraction consist of columnar grains surrounded with interlayer amorphous phase.^{11,12} Columnar grains with a diameter of a few hundred angstroms and a length of a few thousand angstroms grow from near the quartz substrate. The width of the interlayer amorphous phase is several tens of angstroms. At the interface between Cat-CVD poly-Si films and quartz substrate, incubation

amorphous layer of the thickness ranging from a few tens to 200 Å is occasionally observed. However, the thickness of the incubation layer is apparently thinner than that observed for poly-Si films obtained by low-temperature PECVD.¹³ It was also revealed by the Hall measurements that the potential barrier height at the grain boundary in Cat-CVD poly-Si films is quite low, about 7 meV, for the films with crystalline fraction of 90%.¹⁴

In this study, directional anisotropy in electrical conduction for Cat-CVD poly-Si films was observed for the first time. Relationship between the electrical anisotropy and the above-mentioned structural anisotropy with columnar grains is discussed. A novel method to analyze the properties of crystalline and amorphous phases which constitute Cat-CVD poly-Si films is proposed. Then, the results obtained using the proposed method are shown. Obtained electrical properties are compared with structural properties, for example, crystallinity and defect properties. Finally, the quality of Cat-CVD poly-Si films is improved, showing the feasibility of solar-cell applications of the Cat-CVD poly-Si films.

II. EXPERIMENT

A. Preparation of Si films

Sample films were prepared on fused-quartz and Si substrates by Cat-CVD. The native oxide on Si substrates was removed by diluted-HF etching before deposition. Cat-CVD apparatus used in this study is schematically shown in Fig. 1. A gaseous mixture of SiH₄ and H₂ was introduced into the chamber. The flow rate of H₂ was fixed to 30 sccm and that of SiH₄ was varied from 0.5 to 2.5 sccm. The gas pressure during deposition was about 0.16 Pa. The catalyzer made of tungsten (W) was set under the substrates with a distance of 35–40 mm. The area of the catalyzer surface was 46 cm².

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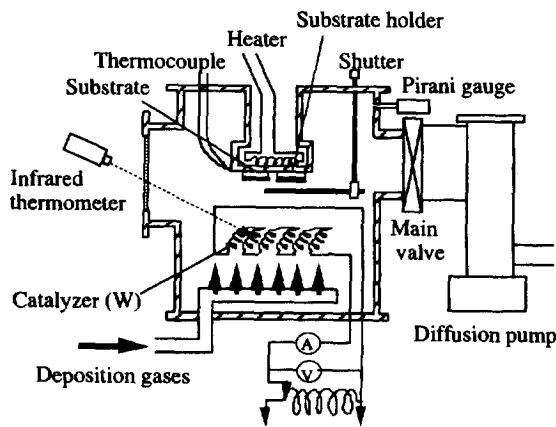


FIG. 1. Schematic diagram of Cat-CVD apparatus.

The electric power supplied to the catalyzer, PW_{cat} , in order to heat it was 1000 W. The temperature of the catalyzer, T_{cat} , measured by a pyrometer was 1600–1700 °C. The substrate temperature was controlled with a heater in the substrate holder. The temperature of substrate surface, measured and corrected with two thermocouples attached to the substrate holder and the substrate surface, was 300–400 °C.

B. Characterization methods for Si films

Crystallinity was evaluated for samples on fused-quartz or Si substrates by Raman scattering spectroscopy at room temperature using an Ar-ion laser with a wavelength of 514.5 nm. Crystalline fraction was estimated quantitatively by separating the transverse optical phonon Raman spectra into three components;¹⁵ signal around 520 cm^{-1} due to crystalline phase with the grain size larger than 10 nm, that at 510–515 cm^{-1} due to crystalline phase with the grain size smaller than 10 nm, and that around 480 cm^{-1} due to amorphous phase. Crystalline fraction was estimated from the ratio of the sum of I_c and I_m , to the sum of I_c , I_m , and I_a , where I_c , I_m , and I_a are integration intensities of crystalline component around 520 cm^{-1} , intermediate component at 510–515 cm^{-1} , and amorphous component around 480 cm^{-1} , respectively.

Hydrogen (H) atoms play an important role in determining properties of *a*-Si and poly-Si. Dangling bonds (DBs) in *a*-Si and poly-Si are passivated with H, however, it is supposed that H has relation to the photodegradation. The H content and Si-H bond configuration were investigated by Fourier transformation infrared absorption (FTIR) spectroscopy for samples on *n*-type (100) Si substrates with the high resistivity of 30–40 Ωcm . The H content was estimated from the absorption signals in FTIR spectrum at 2000 cm^{-1} due to SiH monohydride stretching-mode vibration, 2090 cm^{-1} due to SiH₂ dihydride stretching-mode vibration, and at 630 cm^{-1} due to Si–H wagging-mode vibration. The density of oscillators, N_o , in FTIR absorption spectroscopy is estimated using the equation: $N_o = A \int \alpha(\omega) d\omega / \omega_0$, where, A , α , ω , and ω_0 are proportionality constant, absorption coefficient, angular frequency, and the peak angular frequency of the absorption signal due to the oscillator, respectively.

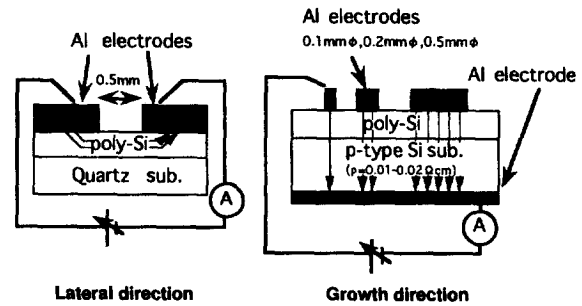


FIG. 2. Sample structures for the conductivity measurements.

The values of A employed in this study are $9.0 \times 10^{19} \text{ cm}^{-2}$ for SiH monohydride stretching-mode vibration,¹⁶ $2.2 \times 10^{20} \text{ cm}^{-2}$ for SiH₂ dihydride stretching-mode vibration,¹⁶ and $2.1 \times 10^{19} \text{ cm}^{-2}$ for Si–H wagging-mode vibration.¹⁶

The direct current electrical conductivity in the growth direction and in the lateral direction of the films was measured in the dark and in a vacuum with a pressure of 10 Pa with changing temperature between 90 and 540 K. Sample structures for the conductivity measurements are shown in Fig. 2. Samples for measurements in the growth direction were deposited on *p*-type (100) Si substrates with the resistivity of 0.01–0.02 Ωcm and had both the top electrodes of Al with the diameters of 0.1, 0.2, and 0.5 mm and the bottom electrode of Al on the backside of Si substrates. Samples for those in the lateral direction were deposited on fused-quartz substrates and had coplanar-type Al electrodes with the gap of 0.5 mm. All the Al electrodes were formed by vacuum evaporation at the background pressure of 10^{-5} Pa. Electrodes with three diameters were used for increasing experimental reliability. Samples with the thickness of 0.3–1.0 μm were used. It was confirmed that the conductivity does not depend on the film thickness in this range. It was also confirmed that the contact resistance is negligibly small by comparing the results in the lateral direction obtained using a four-point probe with those obtained using a two-point probe. Resistance of Si substrate included at the conduction path in the growth direction was considered to be negligible in comparison with the observed resistivity of samples.

The Si-DB density was evaluated from electron spin resonance (ESR) at room temperature in the dark using microwave power of 0.1 mW. Samples on fused-quartz substrates were used for ESR measurements.

III. PROPERTIES OF POLY-SI FILMS ELUCIDATED BY ELECTRICAL ANISOTROPY AND ESR STUDIES

Figure 3 shows both the crystalline fraction and the deposition rate of the films as a function of the flow-rate ratio of SiH₄/H₂. Crystalline fraction of the films increased from 0% to about 90% and the deposition rate decreased to about a quarter with a decrease in the SiH₄/H₂ flow-rate ratio from 8.3×10^{-2} to 1.7×10^{-2} . The difference in the crystalline fraction between the films on Si substrate and those on SiO₂ substrate possibly originates from the difference in the nucleation of the initial layer.¹⁷ It was also found from FTIR mea-

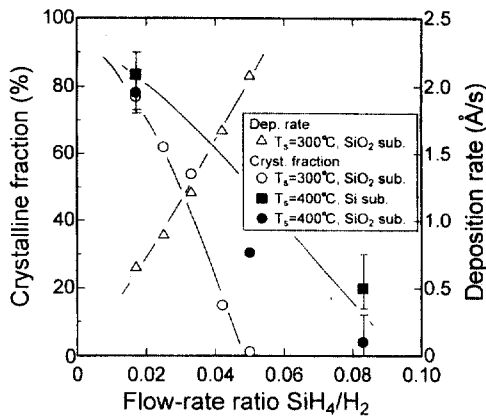


FIG. 3. Crystalline fraction and deposition rate of Si films prepared with PW_{cat} of 1000 W as a function of the flow-rate ratio of SiH_4/H_2 . Triangles show the deposition rate and the other symbols show the crystalline fraction.

measurements that the H content is smaller than 1 at. % and the SiH_2 bonding is dominant regardless of the crystalline fraction.

The DB density estimated by the ESR measurements is shown in Fig. 4 with circular symbols as a function of the crystalline fraction. The ESR results revealed that the spin density is the order of 10^{18} cm^{-3} for the film with the crystalline fraction of 90% and that of 10^{19} cm^{-3} for the film with the crystalline fraction of 0%. The g value of all the samples was about 2.0055, almost equal to that of general α -Si:H prepared by PECVD. It was also found that the shape of ESR spectrum is not changed with an angle between the sample and the magnetic field, suggesting that the DBs exist in the amorphous phase. The decrease in the DB density with a decrease in the volume fraction of the amorphous phase, namely increase in the crystalline fraction, also supports the interpretation that most of DBs are included in the amorphous phase.

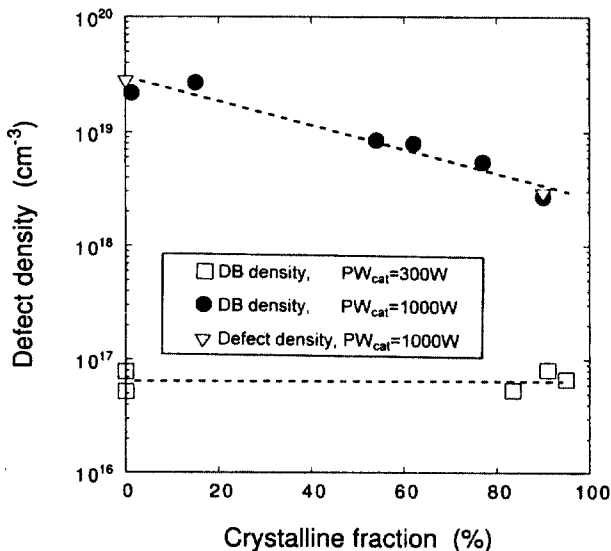


FIG. 4. DB density of Si films prepared with PW_{cat} of 300 and 1000 W as a function of the crystalline fraction. Defect density obtained by electrical measurements for the films prepared with PW_{cat} of 1000 W is also shown.

TABLE I. Average carrier concentration n (Ref. 14) and estimated boundary resistivity ρ_B at various temperature for poly-Si films with the crystalline fraction of 90%.

Temperature T (K)	Average carrier concentration n (cm^{-3})	Boundary resistivity ρ_B ($\Omega \text{ cm}$)
300	1.2×10^{13}	1.5×10^3
350	3.6×10^{14}	5.2×10
400	5.7×10^{15}	3.4

Conductivities in the growth and the lateral directions were found to be different. The directional anisotropy in electrical conduction is probably due to the structural anisotropy observed by TEM. We propose a model of electrical conduction in the two directions, namely in the growth direction and in the lateral direction, for Cat-CVD poly-Si films consisting of columnar structure with high crystalline fraction. Here, we assume that the potential barrier exists at the boundary between crystalline and amorphous phases. According to the model, the conduction path in the growth direction is in parallel of crystalline and amorphous phases, and that in the lateral direction is in series of the crystalline phases, amorphous phases, and the resistivities at the boundaries between the two phases. In the samples for measurements in the lateral direction, the incubation amorphous layer possibly exists at the interface between the films and SiO_2 substrate. However, we consider that the incubation amorphous layer should not be included in the conduction path in the lateral direction because the resistivity of the amorphous layer is usually higher than that of the "bulk" crystalline layer.

According to conventional Seto's theory,¹⁸ the thermionic emission current density J_{te} for an applied voltage V_a across a grain boundary is given by

$$J_{te} \doteq q^2 n V_a (2 \pi m_n^* k_B T)^{-1/2} \exp(-\Phi_B / k_B T), \quad (1)$$

where q is the elementary electric charge, n the average carrier concentration, m_n^* the effective mass of the electron, k_B Boltzmann constant, T the measurement temperature, and Φ_B is the potential barrier height. The conductivity σ of poly-Si films with the grain size L is given by $\sigma = J_{te} L / V_a$. In case that the potential barrier exists at the boundary between crystalline and amorphous phases, V_a and L are transposed by $V_a/2$ and $L/2$. Here, the width of the amorphous phase can be negligible compared with the grain size. Then, the boundary resistivity ρ_B is given by

$$\rho_B \doteq (2/q^2 L n) (2 \pi m_n^* k_B T)^{1/2} \exp(\Phi_B / k_B T). \quad (2)$$

Substituting values of n at various temperatures¹⁴ summarized in Table I, Φ_B of 7 meV¹⁴ and L of 500 Å¹¹ given by measurements into Eq. (1) yields the boundary resistivity ρ_B also shown in Table I. Observed resistivity between $10^5 \Omega \text{ cm}$ at 400 K and $10^7 \Omega \text{ cm}$ at 300 K in the lateral direction was much higher than the boundary resistivity. Therefore the boundary resistivity for the films with the crystalline fraction of 90% is negligibly small compared with that of the amorphous or crystalline phases. It was also confirmed that the boundary resistivity is negligible for the films with the crystalline fraction of 70%. This result suggests that the conduc-

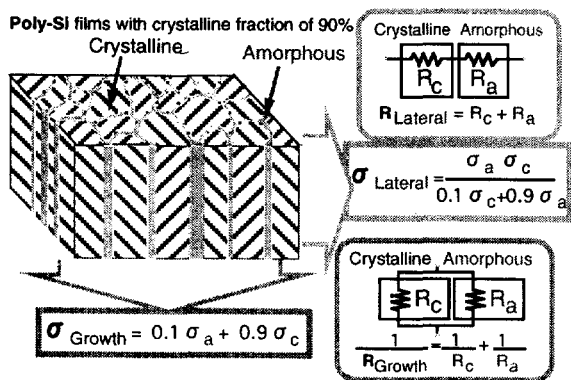


FIG. 5. Conduction model of poly-Si films with the crystalline fraction of 90%.

tion is not dominated by the properties of the grain boundary but by those of the crystalline and amorphous phases.

Therefore, we take the boundary resistivity to be negligible and propose the model of electrical conduction for the films with the crystalline fraction of 90% schematically shown in Fig. 5. The conductivities of crystalline and amorphous phases are given as a function of the conductivities in the two directions as shown in the inset of Fig. 5. Accordingly, the conductivity of each phase is obtained by the observed conductivities in the two directions.

The conductivity of each phase was estimated at various temperatures by the relationship shown in Fig. 5. Arrhenius plots of the estimated conductivity of the crystalline phase for the films with the crystalline fractions of 70% and 90% are shown in Fig. 6. It turns out that for higher crystalline fraction, the thermal activation-type conduction is dominant at lower temperatures. Therefore it is suggested that the crystalline phase with the improved quality is obtained for the films with higher crystalline fraction.

The estimated conductivity of the amorphous phase for the films with the crystalline fractions of 70% and 90% is shown in Fig. 7 as a function of $T^{-1/4}$, together with the observed conductivity of the films with almost no crystalline

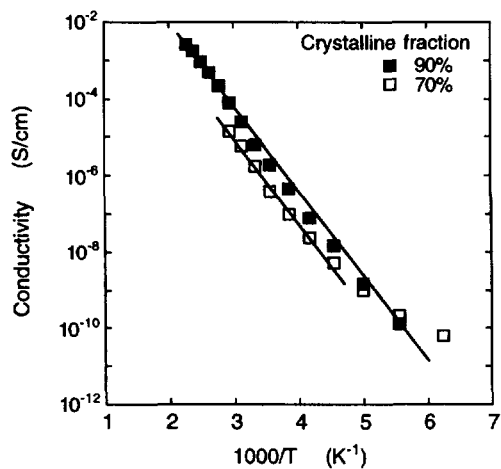


FIG. 6. Arrhenius plots of the estimated conductivity of the crystalline phase for poly-Si films with the crystalline fractions of 70% and 90%.

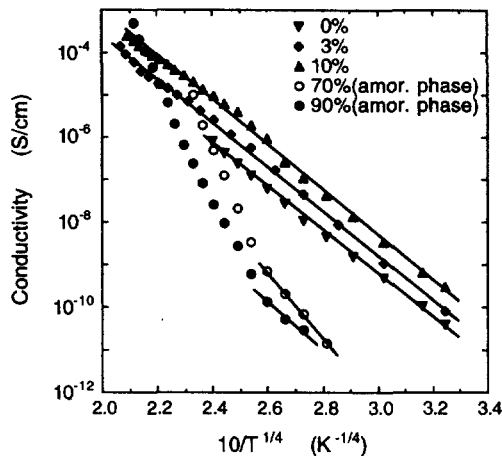


FIG. 7. Conductivity of the amorphous phase for Si films with various crystalline fractions as a function of $T^{-1/4}$.

phase. Here, T is the measurement temperature. It is found that the conduction due to variable-range hopping is dominant even at room temperature for the films with the crystalline fraction of almost 0%, showing that there are a large number of DBs in the films with a large amount of amorphous phase. It is also shown that the conduction due to variable-range hopping is dominant at low temperature regardless of the crystalline fraction. According to the theory of Mott and Davis,¹⁹ the conduction due to variable-range hopping is given by

$$\sigma = \sigma_0 \exp\left(-\frac{B}{T^{1/4}}\right), \quad B = 2.063 \left[\frac{\alpha^3}{k_B N(E_F)} \right]^{1/4}, \quad (3)$$

where $N(E_F)$, α , k_B , T are the density of states at Fermi level E_F , the inverse of localization radius, Boltzmann constant, and the measurement temperature, respectively. Substituting the value of B given by the fitting of measurement points in Fig. 7 and assumed α into Eq. (3) yields the density of states around E_F in the range of 1 eV, which is a measure of the defect density of the samples.

The defect density estimated from the above method is also shown in Fig. 4 with triangular symbols as a function of the crystalline fraction. Here, assuming α^{-1} of 3.5 Å for all the samples, the defect density was estimated to be $2.7 \times 10^{19} \text{ cm}^{-3}$ for the films with the crystalline fraction of 0% and $2.8 \times 10^{19} \text{ cm}^{-3}$ for the amorphous phase in the films with the crystalline fraction of 90%. Since it is considered that the DBs do not exist in the crystalline phase, the defect density of the films given by the electrical measurements is $2.8 \times 10^{18} \text{ cm}^{-3}$ for the films with the crystalline fraction of 90% and is consistent with the DB density measured by ESR, as shown in Fig. 4.

In order to improve the film quality, on the basis of the results from ESR and conductivity measurements, it should be useful to prepare the films under the condition to make the quality of the amorphous phase high.

TABLE II. Preparation conditions for Si films with improved properties.

Substrate	Fused quartz (100) Si
Distance between catalyzer and substrate	50–60 mm
Area of catalyzer surface	6.7 cm ²
T_{cat}	1700 °C
PW_{cat}	300 W
Flow rate of SiH ₄	20/1.5
Flow rate of H ₂	30/100
Gas pressure	0.5 Pa/0.7–2.7 Pa

IV. IMPROVEMENT OF THE QUALITY OF POLY-SI FILMS

It is experimentally known that high quality *a*-Si films are obtained using low PW_{cat} , namely about 300 W, by Cat-CVD for the case when the covered area of the catalyzer wire is about 7 cm×7 cm as in the present case.² Then, we prepared poly-Si films using PW_{cat} equal to that of the preparation condition of high-quality *a*-Si films by Cat-CVD in order to obtain the included amorphous phase with high quality. Preparation conditions are summarized in Table II.

The DB density of the films prepared with PW_{cat} of 300 W is also shown in Fig. 4 with square symbols as a function of the crystalline fraction. The DB density of the films prepared with PW_{cat} of 300 W does not depend on the crystalline fraction. The DB density of the films with the crystalline fraction of 95% is the order of 10¹⁶ cm⁻³, which is smaller by two orders of magnitude than that for the films prepared with PW_{cat} of 1000 W. Poly-Si films with the crystalline fraction larger than 80% and the DB density of the order of 10¹⁶ cm⁻³ were obtained at the deposition rate higher than 1 Å/s. *a*-Si films with the DB density of the order of 10¹⁶ cm⁻³ were obtained at the deposition rate about 10 Å/s. The possible reason for a decrease in the DB density is a decrease in the heat radiation from catalyzer with reducing PW_{cat} in spite of the same T_{cat} . Both long distance between the catalyzer and the substrate and small surface area of the catalyzer are also considered to be available for decreasing the heat radiation.

FTIR spectra of *a*-Si films and poly-Si films with the crystalline fraction of 95% prepared with PW_{cat} of 300 W are shown in Fig. 8. The H content for the films prepared with PW_{cat} of 300 W is about 3 at. % for *a*-Si films and about 1 at. % for poly-Si films. It was also confirmed that the SiH bonding is dominant for *a*-Si films and the SiH₂ bonding is dominant for poly-Si films. It turns out that the DB density is comparatively low in spite of low H content.

V. CONCLUSIONS

It was observed that electrical conduction for Cat-CVD poly-Si films has directional anisotropy. The anisotropy in electrical conduction is thought to originate from the structural anisotropy observed by TEM. Novel method to separately characterize both crystalline and amorphous phases using the electrical anisotropy was proposed. This analysis method was justified by the results of ESR measurements. The obtained results from this analysis suggested that high-

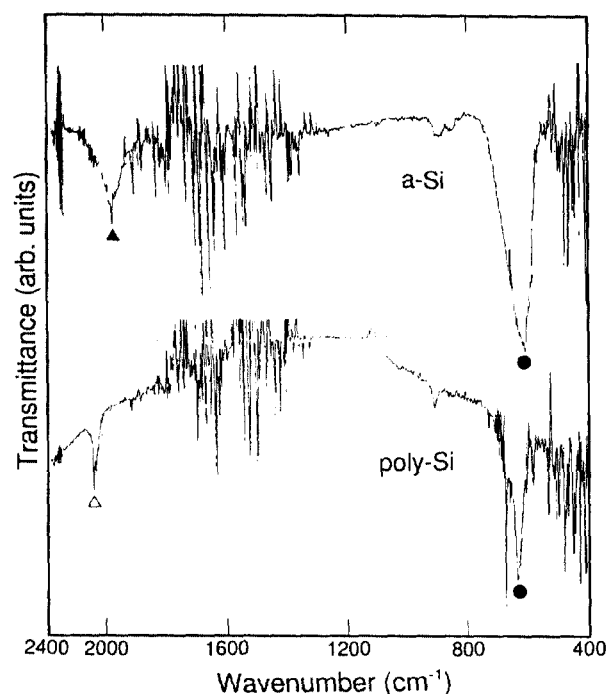


FIG. 8. FTIR spectra of *a*-Si films and poly-Si films with the crystalline fraction of 95% prepared with PW_{cat} of 300 W. Closed circles, closed triangles, and open triangle show Si-H wagging-mode vibration, SiH monohydride stretching-mode vibration, and SiH₂ dihydride stretching-mode vibration, respectively.

quality amorphous phase included is an essential factor in order to obtain high-quality Cat-CVD poly-Si films.

Using PW_{cat} of 300 W, equal to that of the preparation condition of the high-quality *a*-Si films, we succeeded in the preparation of poly-Si films with the crystalline fraction of 95% and the DB density of the order of 10¹⁶ cm⁻³ by Cat-CVD. The reduced DB density is smaller by two orders of magnitude than that of the films prepared with PW_{cat} of 1000 W.

These properties are found to be useful in solar-cell applications of Cat-CVD poly-Si films.

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