Appl. Phys. A 73, 151–159 (2001) / Digital Object Identifier (DOI) 10.1007/s003390100880

Applied Physics A
Materials
Science & Processing

Improvement of transport properties for polycrystalline silicon prepared by plasma-enhanced chemical vapor deposition

T. Kamiya[1,2,*], **A. Suemasu**[3], **T. Watanabe**[4], **T. Sameshima**[4], **I. Shimizu**[3]

[1] Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan
[2] CREST, JST, 3-13-11 Shibuya, Tokyo, 150-0002, Japan
[3] The Graduate School, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8502, Japan
[4] Department of Electrical and Electronic Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Naka-machi, Koganei-city, Tokyo, Japan

Received: 7 August 2000/Accepted: 2 March 2001/Published online: 20 June 2001 – © Springer-Verlag 2001

Abstract. The carrier transport property of polycrystalline silicon (poly-Si:H:F) thin films was studied in relation to film microstructure, impurity, in situ or post-annealing treatments to obtain better carrier transport properties. Poly-Si:H:F films were prepared from SiF_4 and H_2 gas mixtures at temperatures $< 300\,°C$. Dark conductivity of the films prepared at high SiF_4/H_2 gas flow ratio (e.g., 60/3 sccm) exhibits a high value for intrinsic silicon and its Fermi level is located near the conduction band edge. The carrier incorporation is suppressed well, either by in situ hydrogen plasma treatment or by post-annealing with high-pressure hot-H_2O vapor. It is confirmed that weak-bonded hydrogen atoms are removed by the hot-H_2O vapor annealing. In addition, evident correlation between impurity concentrations and dark conductivity is not found for these films. It is thought that the carrier incorporation in the films prepared at high SiF_4/H_2 gas flow ratios is related to grain-boundary defects such as weak-bonded hydrogen. By applying hot-H_2O vapor annealing at 310 °C to a 1-μm-thick *p*-doped (400)-oriented poly-Si:H:F film, Hall mobility was improved from $10\,cm^2/Vs$ to $17\,cm^2/Vs$.

PACS: 73.50.-h; 72.20.-I

Polycrystalline silicon (poly-Si) thin films prepared on inexpensive large-area substrates have attracted much interest because they are expected to be superior materials for giant-microelectronics such as thin film transistors (TFT) for flat panel displays (FPD), solar cells and large-area sensors [1–4]. Especially for TFTs, semiconductor materials with higher mobilities have been sought for higher operation speed. 'Low-temperature polysilicon' TFT displays have already appeared in the market and most of these materials are prepared by laser-anneal re-crystallization of amorphous silicon (a-Si). They can have large field-effect mobilities of over $100\,cm^2/Vs$ (for example, see [5, 6]), that are high enough to integrate the driving circuit onto the same substrate used for the FPD matrix. However, there have been strong demands to reduce fabrication cost and to prepare high-mobility TFT materials without expensive facilities such as an excimer laser.

Micro- or polycrystalline silicon (μc-/poly-Si:H) films prepared by plasma-enhanced chemical vapor deposition (PECVD) from H_2-diluted SiH_4 have demonstrated their ability to prepare high-efficiency solar cells [1]. The advantages of the PECVD are low fabrication cost using low process temperatures ($\leq 300\,°C$) and uniform deposition at large areas. However, the electron Hall mobilities remain rather small, $< 5\,cm^2/Vs$. We have developed a novel technique to prepare large-grain, high-mobility poly-Si:H:F films at low temperatures $\leq 400\,°C$ from gas mixtures of SiF_4 and H_2 [7, 8]. Also, the orientation structure can be controlled by selecting appropriate deposition conditions on glass; e.g., (400)-oriented grains are grown when a SiF_4/H_2 gas flow ratio of 60/3 sccm is used at 300 °C [9, 10]. The fabrication of (400)-oriented poly-Si:H:F films on glass had been a difficult issue for low-temperature processes including laser annealing, despite the fact that the insulator–silicon interface composed of (100) crystallographic surface is a desirable structure to reduce the interface defect density, as is known in silicon MOS TFT technologies. In addition, the (400)-oriented poly-Si:H:F films exhibit large mobilities for low-temperature-prepared μc-/poly-Si films; e.g., electron Hall mobility of $10\,cm^2/Vs$ and free carrier mobility of $40\,cm^2/Vs$ are obtained for the films doped with $10^{20}\,cm^3$-phosphorus atoms [11]. However, these Hall mobility values are still not satisfactory for high-operation-speed devices. And it is a serious problem that undoped (400)-oriented poly-Si:H:F films, which are prepared at high SiF_4/H_2 gas flow ratios such as 60/3 sccm, do not exhibit intrinsic transport properties of crystalline silicon (c-Si); i.e., they display high dark conductivity of $> 10^{-3}\,S/cm$ and its activation energy of $\sim 0.1\,eV$.

*Corresponding author.
Corresponding address: Microelectronics Research Centre, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom.
(Fax: +44-1223/337-706, E-mail: tk257@cam.ac.uk)

In this paper, we study transport properties of poly-Si:H:F films prepared from SiF_4 and H_2 gas mixtures. In particular, we focus on carrier transport in (400)-oriented poly-Si:H:F films and its improvement. First, the structure and transport properties are reviewed in relation to deposition conditions, and then their transport properties are discussed in relation to the microstructure and impurities. We applied in situ and post-annealing techniques to improve carrier transport properties. In addition, controlling factors of carrier transport will be discussed.

1 Experimental

Very high frequency (VHF: 100 MHz) CVD apparatus was used to prepare poly-Si:H:F films from SiF_4 and H_2 gas mixtures with small amounts of SiH_4 to increase film growth rate (see [9] for experimental details). The most important parameters to control film orientation structure are growth temperature and SiF_4/H_2 gas flow ratio. To obtain undoped (400)-oriented poly-Si:H:F, the SiF_4/H_2 gas flow ratio of 60/3 sccm is used at 300 °C and the SiF_4/H_2 gas flow ratio must be reduced as growth temperature is decreased as reported in [10]. All films were prepared on Corning 7059 glass. Some films were in situ doped with PH_3 (1% concentration, diluted with H_2) to facilitate Hall effect measurement.

To improve carrier transport properties, we applied two different techniques; i.e., in situ hydrogen plasma treatment [12] and hot-H_2O vapor post-annealing techniques [13]. In the in situ hydrogen plasma treatment, we used SiF_4/H_2 gas flow ratio of 60/3 sccm at 300 °C for the growth of (400)-oriented poly-Si:H:F thin layer (growth process) and the gas flow ratio was changed to 0/90 sccm for the hydrogen plasma treatment (hydrogen treatment process). The growth process and the hydrogen treatment process were repeated many times to obtain thick films. The period of the hydrogen treatment process (t_H) was fixed at 10 s and that of the growth process (t_D) was varied from 30 s to 90 s.

In the hot-H_2O vapor annealing, the (400)-oriented poly-Si:H:F films were set in an autoclave with 1.3×10^6 Pa H_2O vapor as illustrated in Fig. 1. The samples were heated up to 270 °C or 310 °C and kept for 3 h.

Film structure was studied by X-ray diffraction (XRD) for structure and orientation determination. Impurity concentration was measured by secondary ion mass spectroscopy (SIMS). Thermal desorption spectroscopy (TDS) was also used to determine the temperature dependence of impurities effusion. Carrier transport properties were evaluated from current–voltage characteristics in dark (dark conductivity will be indicated as σ_d in the following sections) and under 100 mW/cm^2 white-light illumination (σ_p). Hall effect measurements were performed as well.

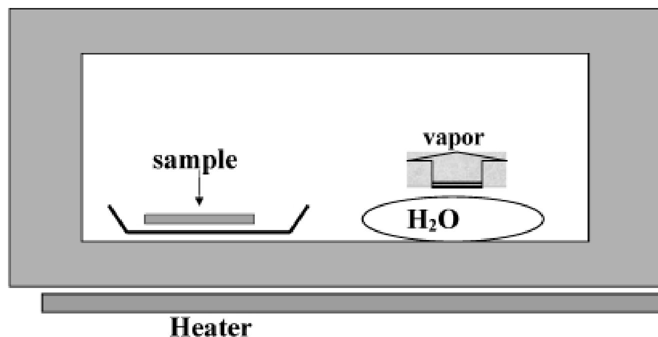


Fig. 1. Schematic illustration of hot-H_2O vapor annealing apparatus

2 Results

2.1 *Structure of* poly-Si:H:F *prepared from* SiF_4/H_2 *gas mixtures*

Figure 2 shows the XRD profiles of undoped poly-Si:H:F films prepared at 300 °C and 200 °C. Gas flow ratios of $SiF_4/H_2 = 60/3$ sccm at 300 °C and 30/14 sccm at 200 °C produce almost complete (400)-oriented poly-Si:H:F films as summarized in Table 1. At smaller SiF_4/H_2 gas flow ratios such as 30/10 sccm, (220)-oriented poly-Si:H:F films are obtained as seen in Fig. 2c.

It should be noted that (220)-oriented poly-Si:H:F are prepared at wide SiF_4/H_2 ratio windows and we can select appropriate deposition conditions to obtain good transport properties as will be shown in the next section. However, the deposition condition window for (400)-oriented poly-Si:H:F films is too narrow to control both the (400)-orientation structure and good transport properties simultaneously (see [10, 12]). Thus we will examine an in situ intermittent plasma treatment and a post-annealing technique to improve transport properties for (400)-oriented poly-Si:H:F films in Sects. 2.4–2.6.

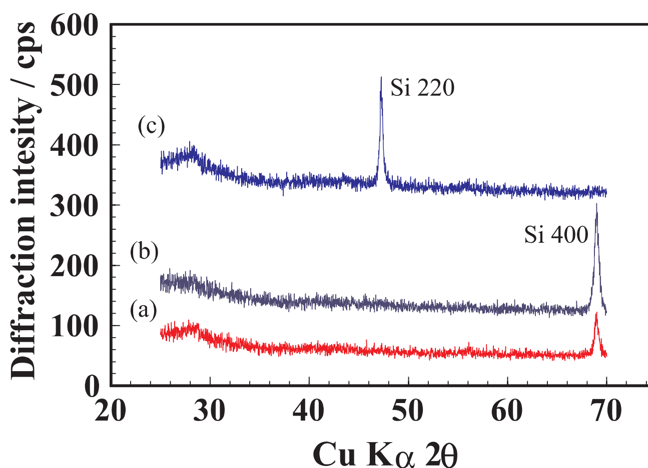


Fig. 2. XRD profiles of poly-Si:H:F films. (400)-oriented poly-Si:H:F film prepared at 300 °C and SiF_4/H_2 of 60/3 sccm (a), (400)-oriented poly-Si:H:F film prepared at 200 °C and SiF_4/H_2 of 30/14 sccm (b), and (220)-oriented poly-Si:H:F film prepared at 300 °C and SiF_4/H_2 of 30/10 sccm (c)

Table 1. Gas flow rates used to grow (400)-oriented poly-Si:H:F films as a function of growth temperature

Ts / °C	SiF_4 / sccm	H_2 / sccm	SiH_4 / sccm
300	60	3.0	0.05
250	30	10	0.1
200	30	14	0.1
150	30	18	0.1

2.2 Transport properties of undoped poly- Si:H:F *films prepared from* SiF_4/H_2 *gas mixtures*

Figure 3 shows σ_d and σ_p of poly-Si:H:F films prepared at 300 °C as a function of the SiF_4/H_2 gas flow ratio. The film orientation structure changes from (400) to a mixture of (220) and (400), and to (220) as the SiF_4/H_2 gas flow ratio decreases. (220)-oriented poly-Si:H:F films are grown at SiF_4/H_2 ratios less than 30 / 10 sccm while reasonably low σ_d for intrinsic silicon (i.e., $< 10^{-6}$ S/cm) are obtained only at smaller SiF_4/H_2 ratios of $\leq 30/40$ sccm; e.g., the film grown at the SiF_4/H_2 gas flow ratio of 30 / 90 sccm exhibits the σ_d value of 6.8×10^{-8} S/cm and the good σ_p value of 1.5×10^{-5} S/cm. However, the σ_d value increases to $> 10^{-3}$ S/cm as the SiF_4/H_2 gas ratio is increased to $> 30/10$ sccm. These results indicate that the high σ_d values obtained at SiF_4/H_2 ratios greater than 30 / 10 sccm are not related to orientation structure.

Figure 4 shows the σ_d and σ_p of (400)-oriented poly-Si:H:F films as a function of growth temperature. As seen in Table 1, smaller SiF_4/H_2 gas flow ratios are needed to grow (400)-oriented poly-Si:H:F films for lower growth temperatures. It can be seen that the σ_d value decreases as growth temperature decreases, though the σ_d of the 200 °C film is still much higher for intrinsic c-Si. This result is consistent with the result obtained in Fig. 3; i.e., the lower growth temperature requires a smaller SiF_4/H_2 gas flow ratio and the decrease in the σ_d with decreasing growth temperature would be attributed to the decrease in the SiF_4/H_2 flow ratio. This result demonstrates that the σ_d value of (400)-oriented film can be reduced by two orders of magnitude by selecting a low growth temperature and low SiF_4/H_2 gas flow ratio conditions, supporting the above conclusion that orientation structure does not control the high σ_d.

The σ_d of the undoped (400)-oriented poly-Si:H:F film prepared at 300 °C is ~ 0.3 S/cm at room temperature and its activation energy (E_a) is low, 0.11 eV (Fig. 5). The E_a value is close to that of σ_p (E_t : 0.093 eV). Since the density of photo-excited carriers is much larger than that of the thermally activated carriers under the illumination condition used for the σ_p measurement, the E_t reflects the activation energy of mobility (E_μ). It is thought that the E_μ (or E_t) reflects potential fluctuations such as barrier height or depth of tail-states of shallow traps at the conduction band edge. From Hall measurements, we observed that the activation energy of carrier density (E_n) was 0.023 eV and the carrier density was $4.3 \times 10^{17}/cm^3$ at room temperature. The E_n corresponds well to the value of $E_a - E_t = 0.017$ eV, supporting the above idea. These results indicate that the Fermi level locates near the conduction band edge and potential fluctuation is ~ 0.093 eV in the undoped (400)-oriented poly-Si:H:F film.

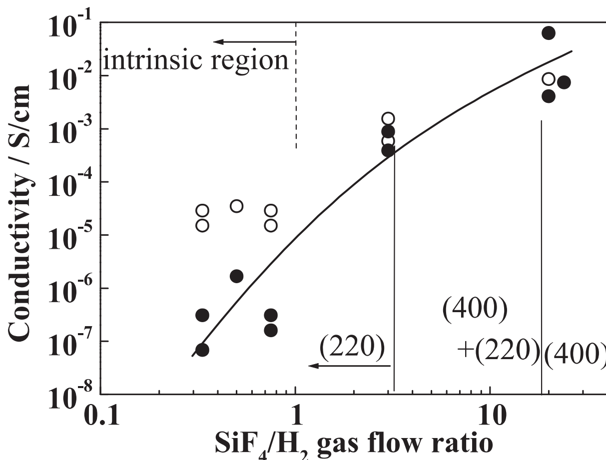


Fig. 3. Conductivity of poly-Si:H:F films prepared at 300 °C as a function of SiF_4/H_2 gas flow ratio. Orientation structure changes from (400) to a mixture of (400) and (220), and to (220) as SiF_4/H_2 gas flow ratio decreases at constant temperature as indicated in the figure. (220) and (400) denote major orientation structure of poly-Si:H:F films obtained at corresponding deposition conditions. *Closed circles*: σ_d, *open circles*: σ_p

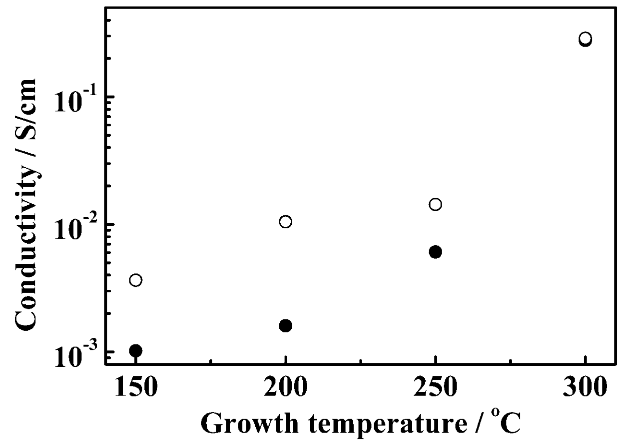


Fig. 4. Conductivity of (400)-oriented poly-Si:H:F films as a function of growth temperature. See Table 1 for deposition conditions. *Closed circles*: σ_d, *open circles*: σ_p

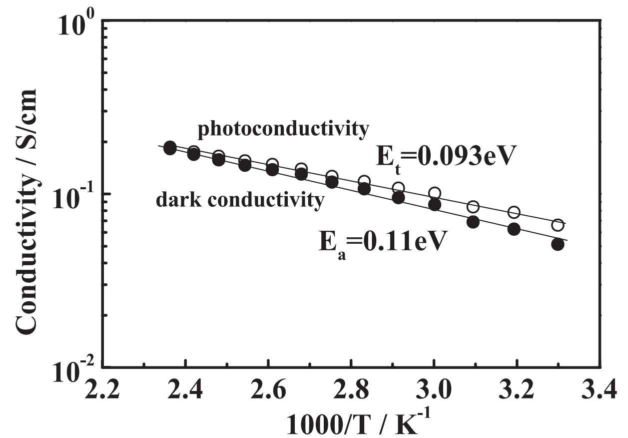


Fig. 5. Temperature dependence of conductivities of undoped (400)-oriented poly-Si:H:F films prepared at 300 °C. *Closed circles*: σ_d, *open circles*: σ_p

2.3 Impurities and transport properties

Shah et al. report that σ_d of μc-/poly-Si:H is significantly affected by impurities (e.g., oxygen) in-diffusion from air [14]. Large σ_d values ($> 10^{-4}$ S/cm) are obtained with films at oxygen concentration (C_O) of $2.2 \times 10^{20}/cm^3$, while it is improved to the order of 10^{-7} S/cm when the C_O is reduced to $2.5 \times 10^{18}/cm^3$. Also, Kamei et al. demonstrate that the use of an ultrapure chamber can reduce the C_O value to $5 \times 10^{16}/cm^3$ and produce intrinsic μc-Si:H films independent of growth temperature [15]. However, even in this case,

the σ_d of μc-Si:H prepared in a conventional (i.e., not ultra-pure) chamber depends on growth temperature and almost-intrinsic films can be obtained at 200 °C. Although the reduction of impurity is favorable, these results suggest that the C_O of $< 10^{18}/cm^3$ would be enough to obtain intrinsic transport properties when the appropriate deposition condition is chosen as seen in Fig. 3. Yet there is another possibility that halogen impurities such as F form donor or acceptor levels in poly-Si:H:F films prepared from fluorinated source gases.

In this section, we examine the relationship between the σ_d and impurity concentrations. As seen in Table 2, both H and F concentrations (C_H and C_F, respectively) are lower for the (400)-oriented poly-Si:H:F films than those of the (220)-oriented poly-Si:H:F films when they are prepared at the same temperature, 300 °C. Also the (400)-oriented poly-Si:H:F films prepared at lower temperatures contain much more F than those prepared at 300 °C. If F atoms form donor or acceptor sites in the film and cause the high σ_d values, these results conflict with the σ_d data shown in Figs. 3 and 4 because the σ_d is lower for (220)-oriented poly-Si:H:F films than for (400)-oriented poly-Si:H:F films.

Table 2. H and F concentrations measured by SIMS for (220)- and (400)-oriented films

Orientation	Growth temperature / °C	F concentration / atoms/cm^3	H concentration / atoms/cm^3
(220)	300	2.1×10^{19}	0.75×10^{21}
(400)	300	0.7×10^{19}	0.57×10^{21}
(400)	200	2.7×10^{19}	1.8×10^{21}

In addition, the σ_d of the (400)-oriented poly-Si:H:F films decreases as growth temperature decreases. In contrast, the C_F value increases as growth temperature decreases. This result indicates that the high σ_d values of the (400)-oriented poly-Si:H:F films cannot be explained by the F incorporation.

Figure 6 shows the relationship between the impurity concentrations measured by SIMS and the σ_d for undoped poly-Si:H:F films prepared at various deposition conditions. As for the C_O, (400)-oriented poly-Si:H:F films exhibit high σ_d values of $> 10^{-3}$ S/cm though the C_O is low, around $2 \times 10^{17}/cm^3$. And reasonably low σ_d values can be obtained

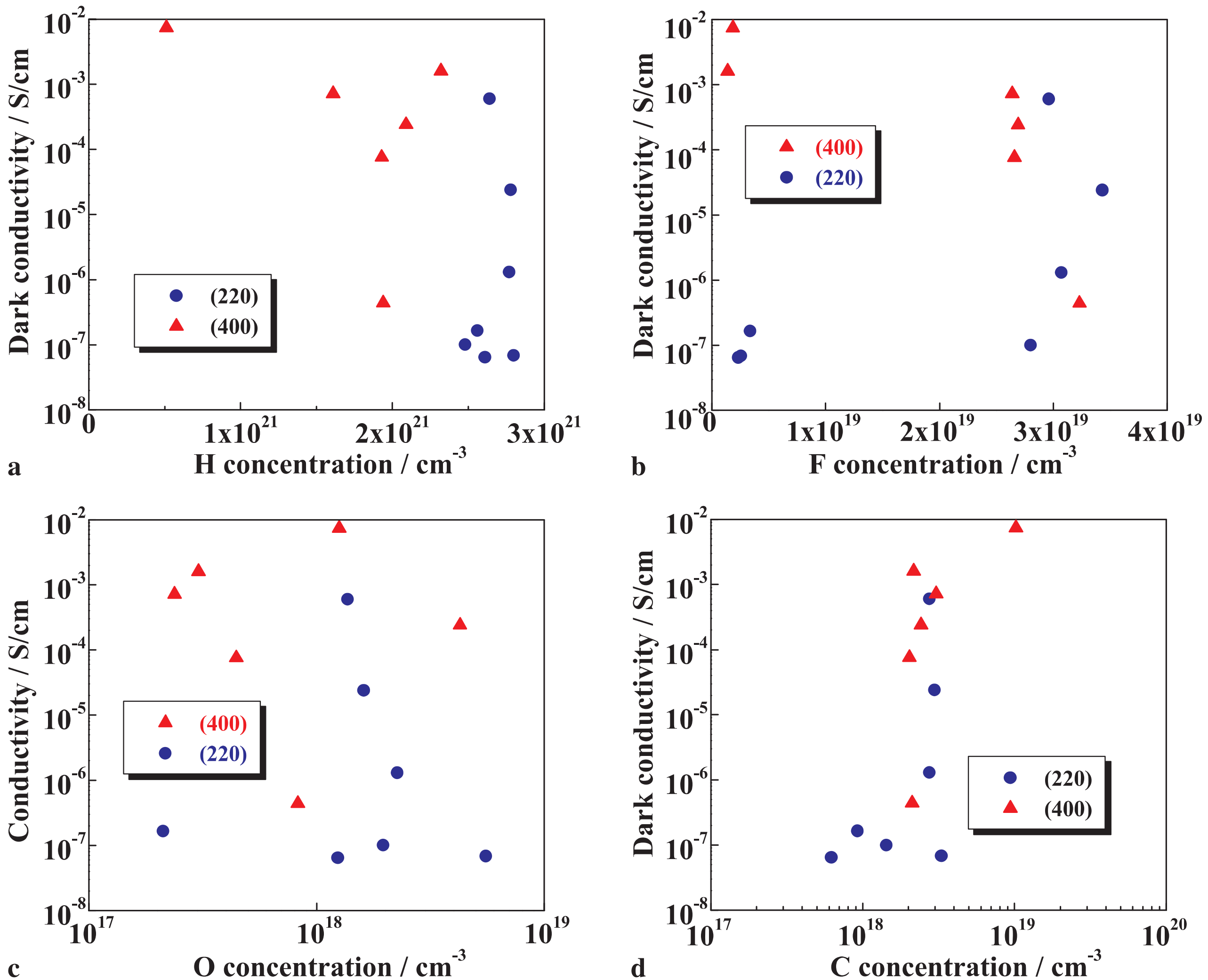


Fig. 6a–d. Relationship between impurity concentrations and dark conductivity for poly-Si:H:F films prepared at various deposition conditions. Impurities are H (**a**), F (**b**), O (**c**), and C (**d**), respectively. Film structures are (220) (*circles*) and (400) orientations (*triangles*)

in wide range of the C_O less than $5\times10^{18}/\mathrm{cm}^3$. Even for other impurities, we cannot find evident relationship between the impurity concentrations and the σ_d value. One may find a trend that the σ_d value of the (400)-oriented poly-Si:H:F films decreases with increasing C_F, however this trend corresponds to the decrease in growth temperature as described above; i.e., lower growth-temperature (400)-oriented poly-Si:H:F films exhibit higher C_F and lower σ_d.

Although the level of the impurity concentrations is high enough to provide carriers with concentration of $4.3\times10^{17}/\mathrm{cm}^3$, a value which is evaluated by room-temperature Hall measurement with the undoped (400)-oriented poly-Si:H:F films prepared at 300 °C, it is unlikely that the high σ_d value of the poly-Si:H:F films prepared at high SiF_4/H_2 gas flow ratio originates from impurity. Also, we confirmed that the (400)-oriented poly-Si:H:F films had crystalline grains with excellent quality from crystallite size measured by XRD, sharpness of Raman scattering spectrum and pseudo-dielectric function peaks, and free carrier mobility measurement [9, 11, 16]. These results lead us to an idea that the high σ_d values and the electron incorporation originate from grain-boundary effects. Possibly, some grain-boundary defects form donor levels.

2.4 Effect of in situ hydrogen passivation for undoped (400)-oriented poly- Si:H:F *films*

In this section, we examine the effect of in situ hydrogen passivation for undoped (400)-oriented poly-Si:H:F films to obtain better intrinsic transport properties. Since the in situ hydrogen treatment is reported in [12] for (400)-oriented poly-Si:H:F films prepared at 200 °C, we briefly explain the result obtained with 300 °C poly-Si:H:F films for comparison with the following hot-H_2O vapor annealing results.

Figure 7 shows the σ_d and the $\sigma_p-\sigma_d$ as a function of the period of the growth process (t_D). We can see that the lowest σ_d value (5×10^{-6} S/cm) is obtained when 10 s of t_H and 60 s of t_D are applied. Although this σ_d value is still high for intrinsic crystalline silicon, it demonstrates that appropriate hydrogen plasma treatment can reduce the σ_d by three orders of magnitude. In the case of the 200 °C film, the σ_d can be reduced to 4.5×10^{-7} S/cm and the E_a was increased to 0.45 eV which is close to half of the band gap (0.55 eV) [12].

2.5 Effect of hot- H_2O *vapor post-annealing for undoped (400)-oriented* poly- Si:H:F *films*

The σ_d and the E_a of undoped (400)-oriented poly-Si:H:F films prepared at 300 °C are improved also by hot-H_2O vapor annealing as seen in Fig. 8. It is found that the E_a is increased to 0.45 eV. Also, Hall effect measurements indicates that carrier density is reduced to less than $10^{13}/\mathrm{cm}^3$. That is, the electron density is reduced by $4.3\times10^{17}/\mathrm{cm}^3$ at room temperature (by $2\times10^{18}/\mathrm{cm}^3$ estimated from the prefactor of the Arrhenius plot of electron density (n_0)). In contrast, the E_t is not changed by the hot-H_2O vapor annealing, indicating that potential fluctuation at the conduction band edge is not affected by the hot-H_2O vapor annealing.

The above results suggest that either the hydrogen plasma treatment or the hot-H_2O vapor annealing can effectively reduce the incorporation of electrons, resulting in the low σ_d and the large E_a. As Shah et al. report [14], oxygen impurity may result in carrier incorporation, however, it is not the case in the hot-H_2O vapor annealing. It is reported that high-quality SiO_x can be formed at ~ 1000 °C by a simple thermal annealing in dry O_2 gas. However, hot-H_2O vapor or O plasma can reduce defect density at much lower temperatures as reported by Sameshima et al. [17, 18]. This indicates that chemically active species such as high-temperature, high-pressure H_2O vapor or O plasma can form high-quality Si−O bonds at low temperatures and O atoms do not act as donors in these cases.

2.6 Effect of hot- H_2O *vapor post-annealing for p-doped (400)-oriented* poly- Si:H:F *films*

In this section, we examine the effect of the hot-H_2O vapor treatment using P-doped poly-Si:H:F films to facilitate Hall effect measurements. Figure 9 shows the Hall measurement results obtained with a 1-µm-thick P-doped (400)-oriented poly-Si:H:F film. The film was prepared under the same

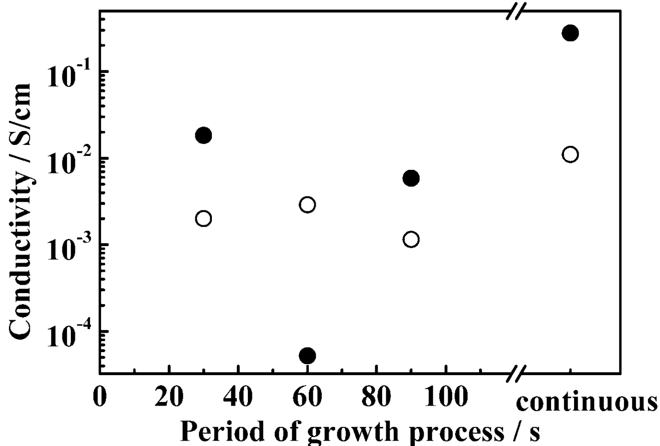


Fig. 7. Conductivities of undoped (400)-oriented poly-Si:H:F films prepared at 300 °C as a function of t_D. *Closed circles*: σ_d, *open circles*: $\sigma_p-\sigma_d$

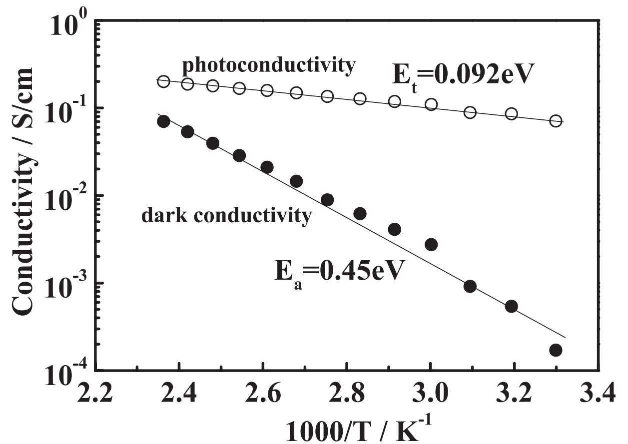


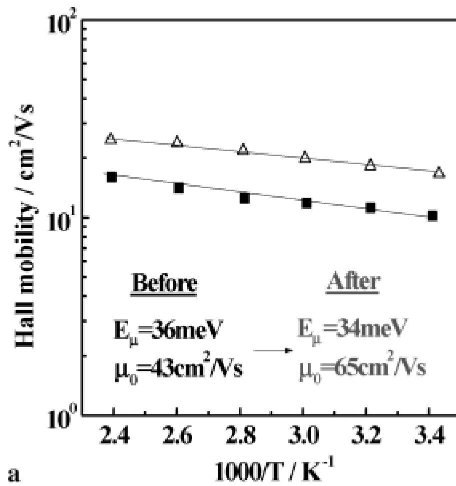
Fig. 8. Dark and photoconductivities of undoped (400)-oriented poly-Si:H:F films prepared at 300 °C after hot-H_2O vapor annealing. *Closed circles*: σ_d, *open circles*: σ_p

conditions used in the previous section. The hot-H_2O vapor annealing was performed at 310 °C for 3 h in this case. The initial Hall mobility is 10 cm^2/Vs at room temperature for the film having electron density of 3.8×10^{18}/cm^3. The E_μ is 36 meV, which is three times smaller than the E_t of the undoped films obtained in Fig. 5. It is known that the potential barrier at grain boundaries is related to defect density below the Fermi energy and carrier density. In addition, energy distributions of shallow traps or band tail may depend on doping concentration and/or Fermi energy. The smaller E_μ of the p-doped poly-Si:H:F film (compared with the undoped film) is consistent with these models.

After the hot-H_2O vapor annealing, the Hall mobility is increased by 70% to 17 cm^2/Vs. It is found that the E_μ is almost the same at 34 meV, while μ_0 is markedly increased from 43 cm^2/Vs to 65 cm^2/Vs. This indicates that the improvement of the Hall mobility is caused by the decrease in grain- boundary resistance and not by the decrease in potential fluctuations.

Also, we found that carrier density was reduced by 6×10^{17}/cm^3 at room temperature (n_{RT}) after the hot-H_2O vapor annealing and the n_0 was reduced by 1.7×10^{18}/cm^3, which correspond well with the carrier density obtained with the undoped (400)-oriented poly-Si:H:F film (4.3×10^{17}/cm^3 and 2×10^{18}/cm^3 for n_{RT} and n_0, respectively). These results suggest that the hot-H_2O vapor annealing successfully suppresses the carrier incorporation, similar to the undoped film case discussed in the previous section.

From SIMS measurements, it is found that H concentration is reduced from 1.0×10^{21}/cm^3 to 0.7×10^{21}/cm^3 by the hot-H_2O vapor annealing (Fig. 10), however, any evident hydrogen removal is not observed by TDS measurement with an as-deposited film (note that the TDS process did not use H_2O vapor) at temperatures less than 310 °C (Fig. 11). This indicates that high-temperature, high-pressure H_2O vapor is chemically active and enhances removal of weak-bonded hydrogen. However, evident changes in O and F concentra-



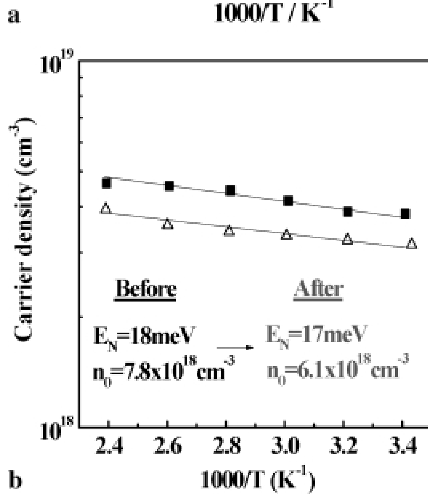
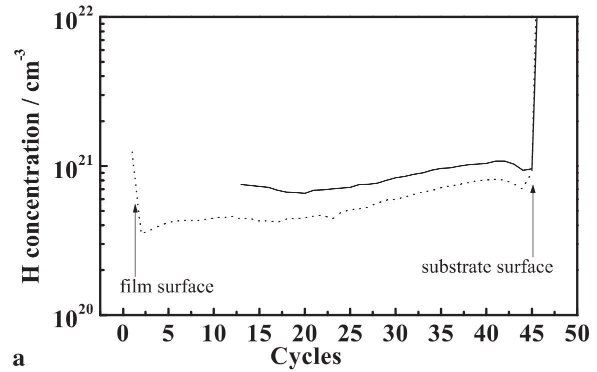
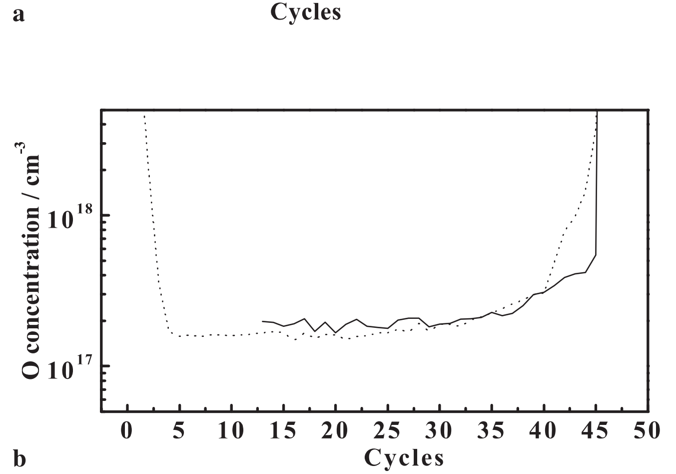


Fig. 9a,b. Hallmobility (**a**) and electron density (**b**) before and after hot-H_2O vapor annealing. *Squares*: as-deposited, *triangles*: after hot-H_2O vapor annealing





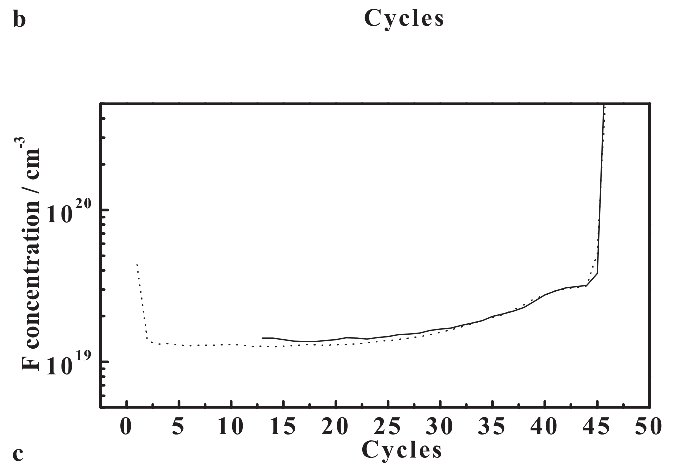


Fig. 10a–c. Impurity concentration depth profiles measured by SIMS. The mass/e ratios correspond to H^- (**a**), O^- (**b**) and F^- (**c**). *Solid lines*: as-deposited film, *dashed lines*: after hot-H_2O vapor annealing

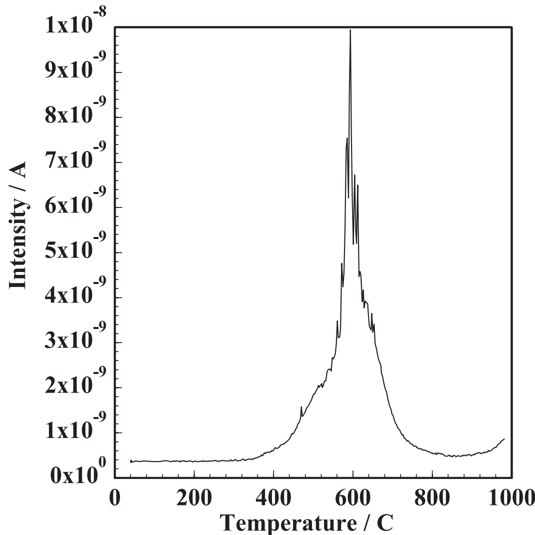


Fig. 11. TDS spectrum at mass/e ratio $= 2$ (corresponds to H_2^+)

tion s by the hot-H_2O vapor annealing are not detected by SIMS, indicating that O incorporation is less than the order of $10^{17}/cm^3$, which is a background-level value of the SIMS apparatus used in this work. As for F, any effusion of F-related clusters such as HF, SiF and SiF_2 are not detected by TDS at temperatures $< 400\,°C$, which is consistent with the SIMS result.

3 Discussion

3.1 Origin of carrier incorporation in undoped (400)-oriented poly-Si:H:F *films*

From the results of Sect. 2.3, we knew that high σ_d values of poly-Si:H:F films relate to deposition conditions such as SiF_4/H_2 gas flow ratio rather than to impurity concentration. Hall measurements revealed that the high σ_d values originate from carrier incorporation, which subsequently result in a high Fermi level. In addition, clear correlation between the high σ_d value and the impurity concentration could not be found.

Especially, it should be noted that (400)-oriented poly-Si:H:F films have low C_O and C_F though they exhibit higher σ_d than those of (220)-oriented poly-Si:H:F films with higher C_O and C_F. These low impurities in the (400)-oriented poly-Si:H:F films can be understood from the fact that incorporation of impurity significantly depends on film structure such as crystal fraction and quality of crystalline grains; e.g., epitaxial film exhibits lower C_F and C_H than those of poly-Si:H:F films by two orders of magnitude when they are grown in the same deposition chamber [19]. As we previously reported, the (400) preferential growth mechanism involves strong selectivity of c-Si(100) surface and selective etching of specific crystallographic planes similar to the epitaxial growth case [16]. Thus it is thought that the low impurity concentrations in the (400)-oriented poly-Si:H:F films are related to the (400) preferential growth mechanism including the selective sticking and the selective etching.

In Sects. 2.4–2.6, it was found that either the in situ hydrogen plasma treatment or the post hot-H_2O vapor annealing decreased the σ_d value and the carrier density in the (400)-oriented poly-Si:H:F films. It was confirmed that evident change in impurity concentrations by the hydrogen plasma treatment was not detected. Whereas hot-H_2O vapor annealing decreased the C_H by $6 \times 10^{19}/cm^3$ but did not result in detectable change of the C_O and the C_F. These results also support the idea that the suppression of the carrier incorporation by the in situ hydrogen treatment and the hot-H_2O vapor annealing is not related to impurity concentration.

However, the above results are puzzling. Generally, hydrogen atoms play an important role in terminating and passivating dangling bonds in a-Si:H and at grain boundaries of μc-/poly-Si. Thus the C_H decrease by the hot-H_2O vapor annealing is usually expected to increase dangling bonds, resulting in deteriorated transport properties. However, as seen in Fig. 9, it does not increase potential fluctuation but increases Hall mobility by the reduction of grain-boundary resistance.

Considering the fact that the dangling-bond density is estimated to be $5.4 \times 10^{20}/cm^3$ for films with columnar grains of 100-nm diameter by assuming each silicon atom at grain boundaries has one dangling bond, $0.7 \times 10^{21}/cm^3$ of C_H obtained with the hot-H_2O vapor-annealed poly-Si:H:F film is still high enough to fully terminate grain-boundary dangling bonds. In addition, from the comparison with the TDS result, it is found that weakly bonded hydrogen atoms are removed by the hot-H_2O vapor annealing, and subsequently resulted in low carrier density. However, the number of effused hydrogen atoms is $3 \times 10^{20}/cm^3$, a number that is much larger than the decrease in the carrier density ($2 \times 10^{18}/cm^3$ estimated from the n_0 value). To understand this result, we must adopt a supposition that only a small portion ($\sim 1\%$) of weak-bonded hydrogen atoms can cause the carrier incorporation. Also in the in situ hydrogen plasma treatment case, weak-bonded hydrogens are expected to be removed by Si−H and/or Si−Si network rearrangement invoked by hydrogen radicals similar to amorphous silicon cases [20].

There is another possible explanation of the decrease in the electron density due to the hot-H_2O vapor annealing. The incorporation of oxygen was estimated to be less than the order of $10^{17}/cm^3$ from SIMS measurement, which is almost equivalent to the decrease in the electron density by the hot-H_2O vapor annealing. Thus grain-boundary dangling bonds would be terminated with oxygen atoms. In the in situ hydrogen treatment case, dangling bonds can be terminated by excess hydrogen supplied during the hydrogen treatment period. The termination with oxygen or hydrogen may reduce the carrier incorporation.

3.2 Mechanism of improvement of Hall mobility by hot-H_2O *vapor annealing*

Sameshima et al. report that as-prepared poly-Si prepared by laser crystallization exhibits poor electric properties [21]; e.g., carrier density measured by Hall effect measurement (n_{Hall}) is of the order of $10^{12}/cm^3$ whereas the phosphorus dose is $1 \times 10^{18}/cm^3$, and carrier density in crystalline grains estimated by free carrier optical absorption technique (n_{FCA}) is $10^{16}/cm^3$. In this case, a potential barrier with height of ~ 0.3 eV is formed at grain boundaries, because the as-deposited poly-Si has defects of the order of $10^{18}/cm^3$ at grain boundaries, which trap electrons to form the potential

barrier. This high potential barrier at grain boundaries inhibits the transport of free electrons across grain boundaries, resulting in the much lower n_{Hall} than n_{FCA}. The potential barrier almost disappears after hot-H_2O vapor annealing at 310 °C. In this case, defect density is decreased to $\sim 1 \times 10^{17}/cm^3$ and both n_{Hall} and n_{FCA} are increased to $\sim 3 \times 10^{17}/cm^3$.

In contrast, as-deposited P-doped poly-Si:H:F films prepared by PECVD exhibit $3.8 \times 10^{18}/cm^3$ of electron density as seen in Fig. 9 and ionization efficiency was estimated to be $\sim 50\%$ from SIMS result. After the hot-H_2O vapor annealing at 310 °C, the carrier density is decreased by $6 \times 10^{17}/cm^3$, a value that almost corresponds to carrier incorporation of the undoped film. Potential fluctuation was not affected by the hot-H_2O vapor annealing. This discrepancy with the result obtained with the laser-crystallized poly-Si is thought to originate from H termination of grain-boundary defects in the poly-Si:H:F films prepared by PECVD. Most of the grain-boundary defects in the poly-Si:H:F films are in situ passivated with H atoms during the deposition, which decrease defect density and form grain boundaries with small potential fluctuation of ~ 36 meV. This small potential fluctuation does not significantly perturb carrier transport across grain boundaries. Thus higher n_{Hall} is obtained with the as-deposited poly-Si:H:F films than those of the as-prepared laser-crystallized poly-Si films.

It is more important to note that the Hall mobility of the poly-Si:H:F film is improved to $17\,cm^2/Vs$ by the hot-H_2O vapor annealing. This Hall mobility value is high for μc-/poly-Si films prepared by PECVD at low temperatures < 400 °C with the same film thickness of 1 μm. We previously reported that Hall mobilities of poly-Si:H:F films were controlled by grain boundary effects [11]; i.e., either grain-boundary potential fluctuation or grain-boundary resistance decreased the Hall mobility. After the hot-H_2O vapor annealing, the E_{μ} is not changed largely, whereas the prefactor μ_0 is increased. This result suggests that the Hall mobility results from the decrease in grain-boundary resistance induced by hot-H_2O vapor annealing.

As described above, many grain-boundary defects are terminated with H atoms in poly-Si:H:F films. In this case, the wave function of Si−H bonds is thought to be localized at a grain boundary and not extended to the neighboring crystal grains. This may reduce carrier mobility at grain boundaries. In contrast, it is expected that divalent atoms such as O can terminate dangling bonds located at neighboring grains and inter-link each grain, resulting in larger mobility and/or larger tunneling probability at grain boundaries. Alternatively, the chemically active hot-H_2O vapor removes weak-bonded hydrogen atoms. It is expected that such hydrogen extraction can cause structural relaxation in silicon networks at grain boundaries similar to the case of so called "chemical annealing" used for band-gap modification of a-Si:H [20]. The formation of a more stable network structure may reduce chemical bond distortion and decrease the local effective mass of carriers at grain boundaries, resulting in increased Hall mobility.

4 Conclusions

Transport properties were studied for poly-Si:H:F films prepared on glass at ≤ 300 °C by PECVD from SiF_4/H_2 gas mixtures. It is found that undoped poly-Si:H:F films prepared at high SiF_4/H_2 gas flow ratio condition exhibit large electron density and large dark conductivity, which are related to neither film structure nor impurity. The carrier incorporation is improved by in situ hydrogen plasma treatment or by post-hot-H_2O vapor annealing. These results suggest that grain boundary defects such as dangling bonds and weak-bonded hydrogen caused the carrier incorporation.

Hall mobility of $10\,cm^2/Vs$, which is a high value for poly-Si:H films prepared by low-temperature PECVD, was obtained with 1-μm-thick P-doped (400)-oriented poly-Si:H:F films. Furthermore, it was improved to $17\,cm^2/Vs$ by the hot-H_2O vapor annealing at 310 °C. The improvement in the Hall mobility was caused by the decrease in grain-boundary resistance. It was thought that the grain-boundary resistance was reduced by inter-linking chemical bonds between neighboring crystalline grains with divalent oxygen atoms and/or structural relaxation induced by chemically active high-pressure hot-H_2O vapor.

It should be noted that although Hall mobilities of poly-Si:H:F films prepared by PECVD are low as described in the introduction, larger mobilities can be obtained with large, high-quality crystalline grains. We have proposed that (400) preferential growth mechanism was closely related to the formation of high-quality crystalline grains and the use of fluorinated source gas was effective in growing large grains. In addition, grain-boundary structure modification further improves carrier transport properties in these polycrystalline materials.

Acknowledgements. We would like to express our thanks to Dr. A. Matsuda and Dr. M. Kondo at Electrotechnical Laboratory (ETL), Japan. They permitted us and assisted us to use TDS equipment. This work is supported by the Japan Science and Technology Corporation (JST) through the core research for evolutional science and technology (CREST) project "Creation of New Electronic and Structural Properties on Nanosilicon Materials for Innovative Electronic Devices".

References

1. J. Meier, S. Dubail, J. Cuperus, U. Kroll, R. Platz, P. Torres, J.A.A. Selvan, P. Pernet, N. Beck, N.P. Vaucher, C. Hof, D. Fischer, H. Keppner, A. Shah: J. Non-Cryst. Solids **227–230**, 1250 (1998)
2. K. Yamamoto, M. Yoshimi, T. Suzuki, Y. Tawada, Y. Okamoto,A. Nakajima: Mater. Res. Soc. Symp. Proc. **507**, 131 (1998)
3. T. Nagahara, K. Fujimoto, N. Kohno, Y. Kashiwagi, H. Kakinoki: Jpn. J. Appl. Phys. **31**, 4555 (1992)
4. T. Sameshima: Appl. Surf. Sci. **96–98**, 352 (1996)
5. T. Sameshima, M. Satoh, K. Sakamoto, K. Ozaki, K. Saitoh: Jpn. J. Appl. Phys. **37**, L1030 (1998)
6. T. Serikawa, S. Shirai, S. Takaoka, K. Murase, S. Ishida: Jpn. J. Appl. Phys. **33**, L409 (1994)
7. D. He, N. Okada, C.M. Fortmann, I. Shimizu: J. Appl. Phys. **76**, 4728 (1994)
8. T. Kamiya, K. Nakahata, K. Ro, C.M. Fortmann, I. Shimizu: Mater. Res. Soc. Symp. Proc. **557**, 513 (1999)
9. T. Kamiya, K. Nakahata, A. Miida, C.M. Fortmann, I. Shimizu: Thin Solid Films **337**, 18 (1999)
10. T. Kamiya, K. Nakahata, C.M. Fortmann, I. Shimizu: J. Non-Cryst. Sol. **266–269**, 120 (2000)
11. T. Kamiya, K. Nakahata, T. Sameshima, T. Watanabe, T. Mouri, I. Shimizu: J. Appl. Phys. **88**, 3310 (2000)
12. A. Suemasu, K. Nakahata, K. Ro, T. Kamiya, C.M. Fortmann, I. Shimizu: Solar Energy Mater. Solar Cells **66**, 313 (2001)
13. T. Sameshima, M. Satoh, K. Sakamoto, K. Ozaki, K. Saitoh: Jpn. J. Appl. Phys. **37**, L1030 (1998)

14. P. Torres, J. Meier, R. Fluckiger, U. Kroll, J.A. Anna Selvan, H. Keppner, A. Shah, S.D. Littlelwood, I.E. Kelly, P. Giannoules: Appl. Phys. Lett. **69**, 1373 (1996)
15. T. Kamei, M. Kondo, A. Matsuda: Jpn. J. Appl. Phys. **37**, L265 (1998)
16. T. Kamiya, K. Nakahata, K. Ro, C.M. Fortmann, I. Shimizu: Jpn. J. Appl. Phys. **38**, 5750 (1999)
17. T. Samshima, M. Satoh, K. Sakamoto, K. Ozaki, K. Saitoh: Jpn. J. Appl. Phys. **37**, 4254 (1998)
18. Y. Tsunoda, T. Sameshima, S. Higashi: Jpn. J. Appl. Phys. **39**, 1656 (2000)
19. T. Akasaka, D.He.Y. Miyamoto, N. Kitazawa, I. Shimizu: Thin Solid Films **296**, 2 (1997)
20. W. Futako, T. Kamiya, C.M. Fortmann, I. Shimizu: J. Non-Cryst. Sol. **266**-**269**, 630 (2000)
21. K. Asada, K. Sakamoto, T. Watanabe, T. Sameshima, S. Higashi: Jpn. J. Appl. Phys. **39**, 3883 (2000)