AIP Applied Physics Letters

Change in crystalline morphologies of polycrystalline silicon films prepared by radiofrequency plasmaenhanced chemical vapor deposition using SiF4+H2 gas mixture at 350°C

Toshiki Kaneko, Masatoshi Wakagi, Kenichi Onisawa, and Tetsuroh Minemura

Citation: Appl. Phys. Lett. **64**, 1865 (1994); doi: 10.1063/1.111781
View online: http://dx.doi.org/10.1063/1.111781
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v64/i14
Published by the American Institute of Physics.

Related Articles

Mobility enhancement of strained Si by optimized SiGe/Si/SiGe structures
Appl. Phys. Lett. 101, 042111 (2012)

Transport characteristics of AlGaN/GaN/AlGaN double heterostructures with high electron mobility
J. Appl. Phys. 112, 023707 (2012)

Nitrogen-polar core-shell GaN light-emitting diodes grown by selective area metalorganic vapor phase epitaxy
Appl. Phys. Lett. 101, 032103 (2012)

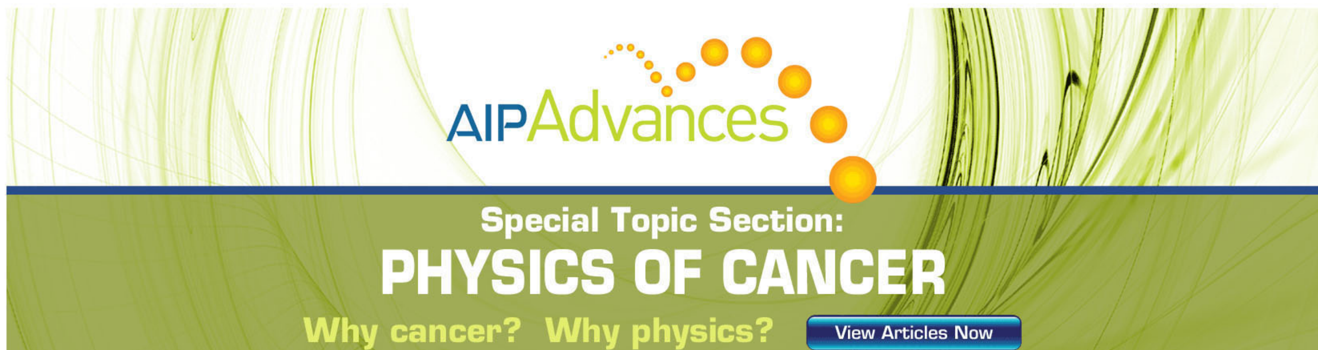
Illumination effects on electrical characteristics of GaN/AlGaN/GaN heterostructures and heterostructure field effect transistors and their elimination by proper surface passivation
J. Appl. Phys. 112, 014511 (2012)

Growth and characterizations of semipolar (112) InN
J. Appl. Phys. 112, 013530 (2012)

Additional information on Appl. Phys. Lett.

Journal Homepage: http://apl.aip.org/
Journal Information: http://apl.aip.org/about/about_the_journal
Top downloads: http://apl.aip.org/features/most_downloaded
Information for Authors: http://apl.aip.org/authors

ADVERTISEMENT



Downloaded 28 Jul 2012 to 114.70.10.202. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions

Change in crystalline morphologies of polycrystalline silicon films prepared by radio-frequency plasma-enhanced chemical vapor deposition using SiF_4+H_2 gas mixture at 350 °C

Toshiki Kaneko, Masatoshi Wakagi, Ken-ichi Onisawa, and Tetsuroh Minemura
Hitachi Research Laboratory, Hitachi, Ltd. 7-1-1 Ohmika-cho, Hitachi-shi, Ibaraki 319-12, Japan

(Received 19 April 1993; accepted for publication 30 November 1993)

Polycrystalline silicon films have been deposited on glass substrates at 350 °C by radio-frequency plasma-enhanced chemical vapor deposition using a SiF_4+H_2 gas mixture. Crystalline fraction decreased abruptly with increasing gas flow ratio. Film structure drastically changed by increasing gas pressure from 0.4 to 2.0 Torr. At lower gas pressure, columnar crystals 30 nm in diameter grew from the glass substrates, while at higher gas pressure larger columnar crystals with a maximum diameter of approximately 100 nm grew on an amorphous Si layer approximately 170 nm thick.

In order to realize high performance thin film transistors for active-matrix liquid crystal displays with low production cost, it is desirable that polycrystalline silicon films are prepared at a temperature low enough to utilize inexpensive glass substrates. Several plasma-enhanced chemical vapor deposition (PECVD) methods have been proposed to achieve such an object. These include several conventional radio-frequency (rf) PECVD methods using monosilane (SiH_4) and hydrogen (H_2),[1–3] using SiH_4 and silicon tetrafluoride (SiF_4),[4,5] and using SiF_4 and H_2 gas mixtures.[6] Some other PECVD methods are under consideration such as the pulsed silane flow method,[7] remote plasma CVD,[8] and microwave PECVD using SiF_4+H_2 gases.[9]

In these studies, it is recognized that heavy dilution of SiH_4 with H_2 causes microcrystallization of silicon films.[1–3] Furthermore, exposure of amorphous silicon films to hydrogen radicals also leads to formation of microcrystalline silicon (μc-Si) films.[7] Hydrogen radicals are an essential media to induce crystallization of silicon films, because hydrogen radicals helps structural relaxation in the long-range order or rearrangement of absorbed species which leads to crystal nucleation. However, both the crystalline fraction, X_c, and crystalline size are still small as long as the SiH_4 and H_2 gas mixture are used for source gases. This is considered to be due to a low crystal growth rate, because the deposition rate is generally low[1–3] when a SiH_4+H_2 gas mixture is used for μc-Si fabrication, although hydrogen radicals can promote microcrystallization.

It is expected that polycrystalline silicon films with a larger crystalline fraction, X_c, and crystalline size can be obtained by controlling crystal nucleation and crystal growth during deposition, even at low temperatures, for example, 300–350 °C. Suppression of crystal nucleation frequency and increase in crystal growth rate should cause polycrystalline silicon films with good crystallinity, because crystal nucleations followed by rearrangement of absorbed species would hinder the crystal growth.

We have attempted to use fluorine radicals to realize this goal. The strong affinity of fluorine with hydrogen can reduce the crystal nucleation frequency on a film surface since the amount of hydrogen radicals could be decreased by forming hydrogen fluoride. Furthermore, fluorine is expected to increase the crystal growth rate, because fluorine could form the precursor, SiF_2H, which is produced by the collision between Si fragments, SiF_n, and hydrogen radicals, and contribute to an increase in the deposition rate of Si films.[10]

In this letter, we used a SiF_4+H_2 gas mixture—one of the three alternatives SiH_4+F_2, SiF_4+SiH_4, and SiF_4+H_2. This combination eliminates the explosive SiH_4. We intended to achieve good crystallinity polycrystalline silicon films using SiF_4+H_2 gas mixture at 350 °C by conventional rf (13.56 MHz) PECVD. We report a drastic change in crystalline morphology with change in deposition parameters.

The films approximately 300 nm thick were deposited on glass substrates (HOYA NA40) at 350 °C by a capacitively coupled parallel-plate electrode reactor. The gas flow ratio, $V(SiF_4)/[V(SiF_4)+V(H_2)]$, and the gas pressure were varied from 0.25 to 0.9 and from 0.4 to 2.0 Torr, respectively. Radio-frequency power density was fixed at 0.2 W/cm^2.

The crystalline fraction of samples were investigated by Raman scattering method. An Ar^+ laser with 488-nm line was used for an excitation source. The Raman spectrometer was a double monochromator (Jobin Yvon HR-1000) equipped with a cooled photomultiplier and a digital photon counting system. In order to investigate nonuniformity of crystallinity, the Raman spectra were measured from both the top and bottom surfaces of the films. By using the least-squares fitting method, the TO (transverse optical phonon) mode spectra were decomposed into three peaks; a crystalline peak (520 cm^{-1}), an amorphous peak (480 cm^{-1}), and an intermediate peak (about 510 cm^{-1}). The intermediate peak is considered to be caused by the size effect of crystalline phases smaller than 10 nm.[11] The crystalline fraction, X_c, was determined from the following equation,[12]

$$X_c=\frac{I_c+I_m}{I_c+I_m+\sigma I_a}. \tag{1}$$

Here, I_c, I_a, and I_m are integrated intensities of the crystalline, amorphous, and intermediate peaks, respectively, and σ is the ratio of integrated Raman cross section for amorphous phase to crystalline phase. The value was chosen to be one based on the previous analysis.[12]

The films were also analyzed by x-ray diffraction method. Average crystalline size was determined from the value of full width at half-maximum (FWHM) of (110) and (111) diffraction lines by Scherrer's formula.[13] The film structures were also characterized by a Hitachi transmission electron microscope (model H-800).

0003-6951/94/64(14)/1865/3/$6.00
© 1994 American Institute of Physics

Downloaded 28 Jul 2012 to 114.70.10.202. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions

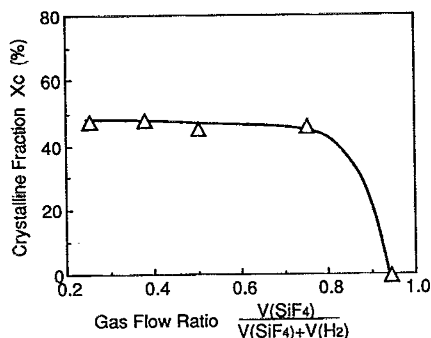


FIG. 1. Crystalline fraction X_c as a function of gas flow ratio. Substrate temperature, total flow rate, and gas pressure are fixed at 350 °C, 120 sccm, and 0.2 Torr, respectively.

Figure 1 shows the crystalline fraction, X_c, as a function of the gas flow ratio. Gas pressure and total flow rate are fixed at 0.2 Torr and 120 sccm, respectively. X_c is almost constant with the increase in the gas flow ratio until 0.75. As the gas flow ratio increases from 0.75 to 0.9, X_c rapidly decreases and an entirely amorphous Si film is deposited at 0.9.

It is clear that the abrupt decrease in X_c shown in Fig. 1 is caused by the decrease in crystal nucleation frequency. This is due to the decrease in amount of hydrogen as well as the increase in fluorine in the rf plasma. Furthermore, it is plausible that the decrease in the number of hydrogen radicals caused by HF formation reaction contributes to the decrease in crystal nucleation frequency.

However, it is found that the values of FWHM of Raman spectra of the films are comparable to that of microcrystalline Si deposited by hydrogen dilution method, indicating that the crystalline size is still small. This is probably due to the low deposition rate, namely from 2 nm/min to 8 nm/min when gas flow ratio is varied from 0.25 to 0.9 in Fig. 1. In order to obtain much higher deposition rate for predominantly crystalline growth, we attempt to increase density of gas molecules by increasing gas pressure at the gas flow ratio of 0.75, at which the crystal nucleation frequency begins to decrease.

Figures 2(a)–2(c) show deposition rate, crystalline fraction, X_c, and crystalline size, respectively, as a function of gas pressure in the range from 0.4 to 2.0 Torr at the total flow rate of 360 sccm. In Fig. 2(a), the deposition rate increases sharply with increasing the gas pressure. The rate at 2.0 Torr is 35 nm/min, approximately ten times that at 0.4 Torr. This is due to the fact that the number of precursors is drastically increased with gas pressure as predicted before. Furthermore, in the lower gas pressure region, fluorine radicals, which do not form precursors contribute to suppression of deposition rate by etching of silicon films. Therefore, it can be concluded from the above, that the deposition rate increases more than linearly with increasing pressure.

From Fig. 2(b), we find two distinct crystalline morphologies. The characteristics of these morphologies are described as follows. (1) Pressure region lower than 0.7 Torr: The X_c measured from the top surface, $X_c(s)$, and that from the bottom surface, $X_c(b)$, are almost the same or their differences are small. This shows that the structure does not change much in the direction perpendicular to the substrate plane. X_c are in the range from 50% to 80%. Crystalline sizes evaluated from (110) and (111) diffraction lines are 34 and 20 nm, respectively. (2) Pressure region higher than 0.7 Torr: $X_c(s)$ is approximately 50%, whereas $X_c(b)$ is less than 5%. This can be explained by a stacked film structure with a top polycrystalline silicon layer and a bottom amorphous Si layer. Crystalline size increases with the increase in gas pressure. At the gas pressure of 2.0 Torr, the values from (110) and (111) diffraction lines become approximately 50 and 30 nm, respectively.

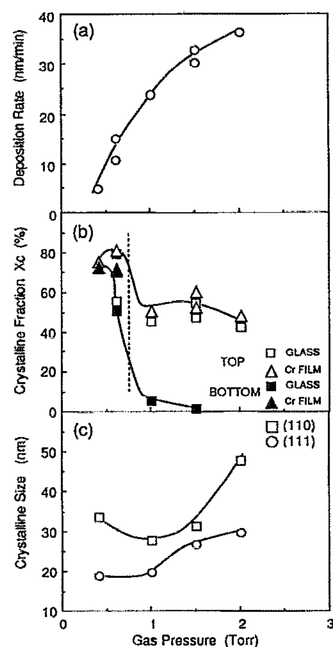


FIG. 2. Relation between gas pressure and (a) deposition rate, (b) crystalline fraction, and (c) crystalline size. Crystalline size was evaluated from Scherrer's formula. Substrate temperature, total flow rate, and gas flow ratio are fixed at 350 °C, 360 sccm, and 0.75, respectively.

The morphologies of deposited films are observed by transmission electron microscopy (TEM). Figures 3 and 4 show dark field images of cross sections of films deposited at

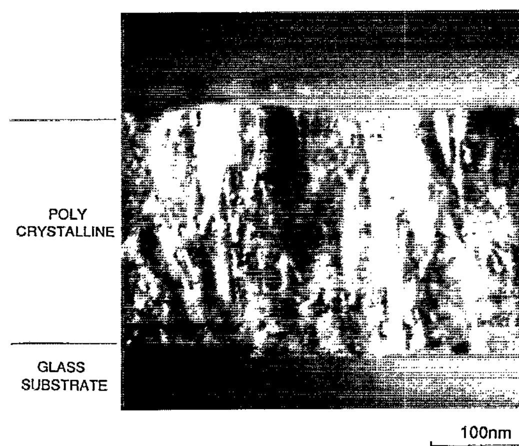


FIG. 3. Dark field image of cross section of the Si film deposited at 0.4 Torr.

Downloaded 28 Jul 2012 to 114.70.10.202. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions

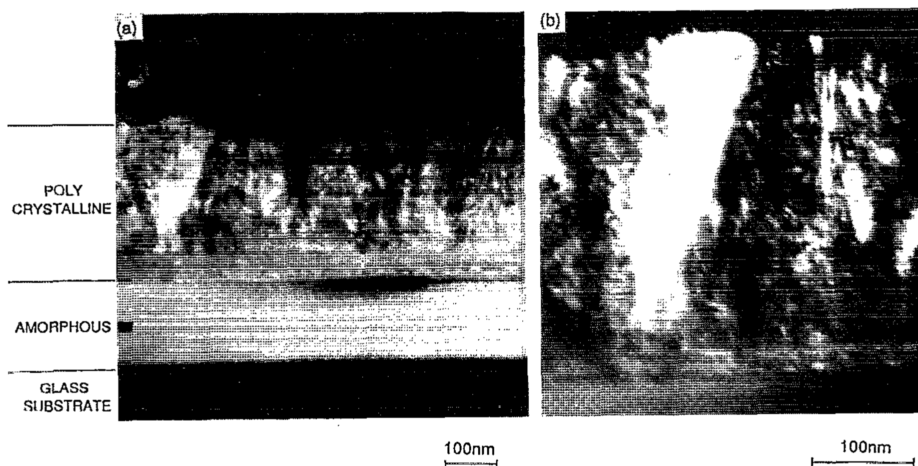


FIG. 4. Dark field image of cross section of the Si film deposited at 2.0 Torr. (a) The image of the whole film which consists of amorphous and crystalline phase. (b) Detailed image of polycrystalline phase.

the gas pressures of 0.4 and 2.0 Torr, respectively. These images were taken from areas with polycrystalline ring patterns. From Fig. 3, it is demonstrated that at 0.4 Torr crystal nucleation occurs from the surface of the glass substrate and columnar crystals grow in the direction perpendicular to the substrate surface. The average diameter of the columns is approximately 30 nm. Figure 4(a) shows that at 2.0 Torr an amorphous phase exists just on the glass substrate as we expect from the results of Raman scattering. The thickness of the amorphous Si layer is approximately 170 nm. Above the amorphous Si layer, we observe columnar crystalline phases with much larger diameters than that deposited at 0.4 Torr. Figure 4(b) shows a detailed photograph in the crystalline phase area with the same magnification as Fig. 3. The diameter increases with the increase in film thickness, and the maximum diameter is approximately 100 nm in the observed area.

The reason of the drastic change in crystalline morphology with respect to gas pressure is discussed next. The formation of amorphous Si phase just above the glass substrate as shown in Fig. 4(a) is due to the decrease in the crystal nucleation frequency. As discussed in Fig. 1, it is considered that the decrease in crystal nucleation frequency is caused by the decrease in hydrogen radicals. On the other hand, the fact shown in Fig. 2(a) that the deposition rate increases with the increase in gas pressure should show the increase in the amount of the precursor, SiF_2H,[10] with respect to gas pressure. From the above consideration, it is suggested that the origin of the drastic change of crystalline morphologies is a significant decrease in hydrogen radicals caused by the increase in collision frequency with gas pressure. Namely, in the lower pressure region, the large amount of hydrogen radicals contribute to crystal nucleation at the beginning of the film deposition. In higher pressure region, hydrogen radicals are consumed to form precursors and hydrogen fluoride molecules. As a result, the amorphous phase grows on the glass substrate since little crystallization due to hydrogen radicals occurs. Once a small amount of crystal nucleation occurs, large diameter crystalline phase can grow predominantly due to the higher growth rate.

The amount of impurities, such as carbon and oxygen, of the film prepared at 0.4 Torr is 3×10^{19} atoms/cm^3 which is approximately three times larger than that of the film prepared at 2.0 Torr, 9×10^{18} atoms/cm^3. It is considered that the impurities of crystalline films as well as the crystalline nucleations maybe impede grain growth especially at lower gas pressure region.

In conclusion, for the first time, we have deposited polycrystalline silicon films on glass substrates at 350 °C by rf PECVD using a SiF_4+H_2 gas mixture. We have shown that polycrystalline silicon films with large crystalline size were achieved by suppressing crystal nucleation frequency and enhancing deposition rate. The film structure changed drastically with the increase in gas pressure. At lower gas pressure, columnar crystals with 30 nm in diameter grew from the glass substrates, on the other hand, at higher gas pressure, larger size of columnar crystals with the maximum diameter of approximately 100 nm grew above a certain thickness of amorphous Si layer.

The authors are grateful to Dr. N. Kinjo of Hitachi Research Laboratory, Hitachi, Ltd. for advice and encouragement, and Professor I. Shimizu of Tokyo Institute of Technology for useful discussion.

[1] G. C. Tsai, G. B. Anderson, R. Thompson, and Wecker, J. Non-Cryst. Solids **114**, 151 (1989).
[2] J. Kanicki, E. Hansen, D. F. Takamori, and J. H. Griffith, Mater. Res. Soc. Symp. Proc. **149**, 173 (1989).
[3] A. Matsuda, J. Non-Cryst. Solids **59&60**, 767 (1983).
[4] T. Nagahara, K. Fujimoto, N. Kohno, Y. Kashiwagi, and H. Kakinoki, Jpn. J. Appl. Phys. **31**, 4555 (1992).
[5] M. Mohri, H. Kakinuma, M. Sakamoto, and H. Sawai, Jpn. J. Appl. Phys. **30**, L799 (1991).
[6] Y. Okada, J. Chen, I. H. Campbell, P. M. Fauchet, and S. Wagner, J. Non-Cryst. Solids **114**, 816 (1989).
[7] M. Otobe, and S. Oda, Jpn. J. Appl. Phys. **31**, 1948 (1992).
[8] C. Wang, M. J. Williams, and G. Lucovsky, J. Vac. Sci. Technol. A **9**, 444 (1991).
[9] M. Nakata, A. Sakai, T. Uematsu, T. Namikawa, H. Shirai, J. Hanna, and I. Shimizu, Philos. Mag. B **63**, 87 (1990).
[10] N. Shibata, K. Fukuda, H. Ohtoshi, J. Hanna, S. Oda, and I. Shimizu, Jpn. J. Appl. Phys. **26**, L10 (1987).
[11] S. Veprek, F. A. Sarott, and Z. Iqbal, Phys. Rev. B **36**, 3344 (1987).
[12] M. Wakagi, T. Kaneko, K. Ogata, and A. Nakano, Mater. Res. Soc. Symp. Proc. **283**, 555 (1993).
[13] H. P. Klug and L. E. Alexander, *X-Ray Diffraction Procedure* (Wiley, New York, 1954).

Downloaded 28 Jul 2012 to 114.70.10.202. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions