Growth mechanisms of crystallites in the mixed-phase silicon films deposited by low-pressure chemical vapor deposition

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Abstract

The microstructure and growth mechanisms of mixed-phase silicon films deposited on glass substrates by infra-low pressure chemical vapor deposition and low pressure chemical vapor deposition using 20% Si$_2$H$_6$/He gas have been investigated by X-ray diffraction and cross-section transmission electron microscopy. The deposition temperature and pressure were in the range of 560–600°C and below 10 mtorr, respectively. In mixed-phase films, there were two kinds of crystallites: initially deposited pre-existing small irregular (311)-preferred crystallites and conventionally incubated (111)-preferred large elliptic bulk-induced crystallites. The behavior of the former changed depending on the deposition conditions of temperature and pressure. Just above the deposition rate below which a (110) polysilicon film formed, (311)-preferred quasi-columnar growth occurred by surface-induced crystallization. This quasi-columnar growth preserved or strengthened the initial (311) preference and grew with an activation energy of 3.1 eV. A further increase of deposition rate made it difficult to form quasi-columnar growth due to a smaller nucleation density and because surface-induced crystallization was suppressed. Then conventional bulk-induced crystallization became dominant to form a (111) preferred mixed-phase films. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Polycrystalline silicon thin films deposited by low pressure chemical vapor deposition (LPCVD) on glass substrates have received considerable interest in the fabrication of thin film transistors for active matrix liquid crystal displays. For this application, the deposition temperature should be below (less than 600°C) the strain point of the low cost glass substrates. Meanwhile, it is important to understand the effect of deposition conditions on the microstructure of as-deposited films because the heat treatment of deposited films gave rise to somewhat different results, depending on their microstructure [1–5].

In previous works on LPCVD films deposited in the temperature range of 580–640°C using silane, Kamins et al. [6] reported that the transition temperature between amorphous to crystalline phase was strongly dependent on deposition conditions. Bisaro et al. [5] and Joubert et al. [3] studied the structure and the texture of as-deposited silicon films as a function of the deposition temperature and pressure. Voutsas and Hatalis [7] have shown that decreasing the deposition rate under any given temperature led from the deposition of amorphous films to the deposition of mixed-phase films, where the crystallites were embedded in an amorphous matrix, and eventually to the deposition of polycrystalline films. However, little attention has been given to the problem of the formation mechanism of...
crystallites in as-deposited mixed-phase silicon thin films. The effect of low pressure on the structure of LPCVD polycrystalline silicon films has been investigated by many authors and they reported the presence of the ⟨311⟩-preferred mixed-phase between the deposition condition of as-deposited polysilicon and that of amorphous silicon [3–5,8].

According to Voutsas et al. [9–13], Kim et al. [14], and Kretz et al. [15], there are two different crystallites in the mixed-phase film deposited by LPCVD using silane [9–14] and disilane gas [15]. First, small irregular crystallites are formed at the film/substrate interface in the initial deposition process followed by the growth of the crystallites. These pre-existing crystallites are explained in terms of direct nucleation mechanism (specific to a corresponding temperature–pressure range) occurring during the first stages of deposition and whereby, small ⟨311⟩ crystallites are formed at the interface between the substrate and film [15]. Second, after an incubation time for conventional solid-phase crystallization (SPC) [10,11] or for CVD [14], new randomly-nucleated bulk-induced crystallization (BIC) takes place in the amorphous matrix, and their growth also begins to become large elliptic grains. Here, we have defined the incubation time for the CVD process as the time from the onset of deposition to the occurrence of crystallite seeds. Hasegawa et al. [16] discussed the changes in the preferential orientation for samples prepared by SPC. ⟨111⟩ BIC take place in the 600°C annealing of amorphous silicon films deposited above 530°C by LPCVD using disilane. However, thermal behaviors of the mixed-phase silicon films are different. Voutsas et al. [11] asserted that rapid growth of pre-existing crystallites were followed by randomly-nucleated crystallization, and further nucleation of the same type of crystallites with pre-existing crystallites was not found. Kim et al. [14] affirmed that pre-existing crystallites only grew slightly and conventionally incubated elliptic grains were dominant for an annealing time longer than incubation time. Despite later nucleation of incubated elliptic crystallites, their final grain sizes are much larger than those of the former, pre-existing mixed-phase crystallites. Kretz et al. [15] also found that the pre-existing ⟨311⟩-preferred crystallites acted as seeds for local solid-phase epitaxial regrowth and ⟨111⟩-oriented crystallites are nucleated newly in the amorphous phase. Harbeke et al. [4] reported the annealing of weak ⟨311⟩ mixed-phase films deposited at 580°C by LPCVD, resulting in the formation of ⟨111⟩ dominant films, but at 600°C, ⟨311⟩ dominant films persisted. Harbeke et al. even reported [8] stronger ⟨311⟩ films upon 1000°C annealing of phosphorus-doped ⟨311⟩ mixed-phase films deposited at 640°C by LPCVD. Most literature reports assert that accelerated crystallization occurs by the growth of both pre-existing crystallites and random-nucleated crystallites, and the growth of pre-existing crystallites is epitaxial regrowth [5,15] or individual fast growth through the ⟨112⟩ branch [11]. Regrowth of pre-existing crystallites formed at the film/substrate interface is surface-induced crystallization (SIC). SIC is preserved or suppressed depending on the deposition condition and BIC is followed when SIC is suppressed. Different results of the thermal treatment of mixed-phase films were observed and systematic analysis would be needed.

In this work, we have given attention to this aspect and to the effect of deposition conditions on the microstructure of as-deposited mixed-phase films using 20% Si2H6/He gas. Infra-low pressure chemical vapor deposition (ILPCVD) and LPCVD depositions were carried out for the extended period of time to obtain thick films, long enough for BIC of randomly-nucleated crystallites to take place during deposition. We have discussed the growth mechanism of mixed-phase silicon films in relation to the evolution of the two kinds of crystallites and their textures, and the resultant microstructure.

2. Experiments

Pyrolysis of diluted disilane using ILPCVD and LPCVD was performed in a conventional tubular reactor (furnace) for growth on 2×2-cm Corning 1733 glass substrates placed parallel to the flow direction. In the furnace, a quartz tube of 4 cm in inner diameter and 90 cm in length with a uniform ambient temperature zone of approximately 20 cm long was positioned at the center and the quartz boat where the substrates were mounted was in this zone during deposition. Diluted disilane (20% Si2H6/He of purity 99.999%) was used under a range of pressures less than 10 mtorr at temperatures in the range 560–600°C. The background pressure in the reactor was 10⁻³ torr using a rotary pump in LPCVD and 10⁻⁶ torr using turbo molecular pump (Balzers TPU240) in ILPCVD. Due to the high dilution of the source gas and low gas flow rate ranging from 1 to 10 sccm, strong depletion of disilane was expected to occur at the temperature range of ours, and resulted in a significant reduction of the deposition rate. The deposition rate was obtained as the thickness of the films obtained divided by the time of growth, giving an average deposition rate. The thickness was measured by surface stylus (Tencor, Alpha-step 200).

In order to investigate the preferred textures of the films, X-ray diffraction (XRD) peaks were measured with a Rigaku D/Max-B X-ray diffractometer using a CuKα line (λ = 1.542 Å), which was a weighted average of Kα₁ (λ = 1.541 Å) and Kα₂ (λ = 1.544 Å) lines with a tube voltage of 40 kV and a tube current of 80 mA. Cross-section transmission electron microscopy (XTEM) specimens were prepared using a mechanical polishing technique followed by ion-milling. XTEM was
used to characterize microstructure of the silicon thin films. Bright-field and dark-field images were obtained by a transmission electron microscope (Philips C-200) operated at 200 keV.

3. Results and discussion

The increase in deposition rate with gas deposition pressure is shown in Fig. 1a,b. Incubating behaviors for deposition did not show up and an immediate deposition was obtained for all cases. This could be due to the much larger sticking coefficient of disilane compared to silane. The deposition rate showed conventional saturating behavior for ILPCVD and LPCVD. For the case of LPCVD (Fig. 1b), the curve seemed to be far away from saturation, but was expected to be saturated at higher deposition pressures. At a low enough deposition rate, the mass-transfer process was dominant. As is already known, the mass-transfer reaction is preferred in order to obtain as-deposited polysilicon because incoming adatoms can find many sites available and diffuse over a long distance before they arrive at the energetically stable sites [17]. As shown in these figures, at any given deposition temperature, there was a deposition rate above which the films had a mixed-phase, consisting of crystallites embedded in an amorphous-phase matrix. Below these minimum deposition rates for mixed-phase silicon films, as-deposited polysilicon with {220} orientation were obtained and had columnar morphology [18]. Here, we were only interested for mixed-phase silicon films.

The textures of the mixed-phase silicon films were determined from XRD and depicted in Fig. 2 and Fig. 3. In order to quantify the texture of the samples, the orientation factor $R_{hkl}$ was defined as follows:

$$R_{hkl} = \frac{I_{hkl}}{F_{hkl}} \sum_{hkl} \frac{I_{hkl}}{F_{hkl}}$$

where for each diffraction plane (hkl), $F_{hkl}$ is the scattering correction factor and $I_{hkl}$ is the measured intensity corrected by an absorption factor taking into account the fact that the films are not infinitely thick. The normalization for obtaining infinite thickness consists in dividing the measured intensity by the following calibration factor $G_c$ [19]:

$$G_c = 1 - \exp(-2\mu t/\sin\theta)$$
Fig. 2. (a). Orientation factors calculated from XRD pattern vs. deposition pressure curves for films deposited at 560°C, with a deposition time of 600 min by ILPCVD. (b). Orientation factors calculated from XRD pattern vs. deposition pressure curves for films deposited at 600°C, with a deposition time of 192 min by LPCVD.

Fig. 3. (a). Orientation factors calculated from XRD pattern vs. deposition time curves for samples deposited at 580°C by ILPCVD at pressures of 4.6 mtorr (closed symbol) and 5.5 mtorr (open symbol). In this pressure range, (311) texture, indicated by the arrow, is dominant and increases with deposition time. (b). Orientation factors calculated from XRD pattern vs. deposition time curves for samples deposited at 580°C by ILPCVD, at pressures of 6.4 mtorr (closed symbol), 7.3 mtorr (open symbol), and 10 mtorr (+ centered symbol). In this pressure range, (311) texture is suppressed and (111) texture indicated by arrow is dominant and increase with deposition time.
where $\mu$ is the absorption coefficient, $t$ is the thickness of the film, and $\theta$ is the diffraction angle of each peak.

At 560°C in ILPCVD, we obtained mixed-phase films at pressures above 2 mtorr. These films were deposited for 600 min, which was long enough compared to the incubation time (less than 400 min for the case of 560°C annealing of film deposited at 520°C using Si$_x$H$_y$ by LPCVD [15]) and the orientation factors are represented in Fig. 2a as a function of deposition pressure. Fig. 2 shows that mixed-phase films prefer $\langle 311 \rangle$ texture at low pressures and prefer $\langle 111 \rangle$ texture at high pressures. At 600°C in LPCVD, we obtained mixed-phase films at pressures above 60 mtorr. These films were deposited for 192 min, much longer than incubation time (less than 100 min, [15]) at this temperature, and their orientation factors are shown in Fig. 2b as a function of the deposition pressure. At 580°C in ILPCVD, we obtained mixed-phase films at pressures above 4 mtorr. Their texture changes are represented in Fig. 3 as a function of the deposition time for several deposition pressures. As shown in Fig. 3a, $\langle 311 \rangle$-orientation factors were dominant and increased with deposition time at the expense of $\langle 220 \rangle$-orientation factors in the pressure range 4–6 mtorr. The $\langle 111 \rangle$-orientation factors were almost invariant during deposition. The mixed-phase films in this pressure range preserved the $\langle 311 \rangle$-preferred orientation. In the pressure range 6–10 mtorr, the $\langle 311 \rangle$-orientation factors were dominant in early stage, but decreased with deposition time, while $\langle 111 \rangle$-orientation factors increased as shown in Fig. 3b. In other words, the mixed-phase films in this pressure range change their morphology from the $\langle 311 \rangle$-preferred to $\langle 111 \rangle$-preferred structure. The question was why and how does initially $\langle 311 \rangle$-preferred behavior persist or disappear? To answer this we examined XTEM images.

XTEM observations with bright-field and dark-field images provided clear evidence of the formation of Si grains and their shapes. Dark-field images were obtained by $\langle 110 \rangle$ selected area diffraction (SAD) micrographs on one of the crystallites in the film. Typical results of these observations are presented in Figs. 4–6. All $\langle 311 \rangle$-preferred mixed-phases show the moving front of amorphous/crystallite (a/c) interface as shown in the bright-field images (Fig. 4a for 600°C LPCVD; Fig. 5a for 580°C ILPCVD; and Fig. 6a for 560°C LPCVD).
ILPCVD, respectively) and dark-field images (Fig. 4b for 600°C LPCVD and Fig. 5b for 580°C ILPCVD, respectively). A small number of elongated elliptical grains existed in these films, as shown in the bright-and dark-field images. On the other hand, bright-field (Fig. 4c for 600°C LPCVD and Fig. 5c for 580°C ILPCVD, respectively) and dark-field images (Fig. 4d for 600°C LPCVD and Fig. 5d for 580°C ILPCVD, respectively) of the (111)-preferred mixed-phase indicated the behavior of BIC as seen from many elongated elliptical grains in these films. Judging from the thickness of top amorphous layers, amorphous Si layers were first deposited and the growth of elliptical grains followed after a certain waiting time. Thus, this (111)-preferred growth process was BIC, which is a general growth mechanism of SPC. In Fig. 4a,b, deposited at 600°C and 67 mtorr by LPCVD, (311)-preferred film growth is dominant, as seen in Fig. 2b, and the figures show a crystallite layer composed of an irregular shape and upper amorphous part in film structure. The upper amorphous part was confirmed by the diffraction pattern showing a halo. In Fig. 4c,d, deposited at 600°C and 110 mtorr by LPCVD, (111)-preferred film growth was the dominant mechanism, as seen in Fig. 2b, while the initial (311)-preferred crystallites grown from the film/substrate interface were suppressed. Thus, the growth mechanism of the film shown in Fig. 4c cannot be SIC but BIC. Here, randomly-nucleated seeds were crowded in density and fast in growth rate; thus grown crystallites quickly filled the amorphous layer from the film/substrate interface to the upper part, resulting in a columnar-like structure. Fig. 5a,b, deposited at 580°C and 4.6 mtorr by ILPCVD, showed a crystallite layer composed of many irregular shapes and an upper amorphous part in film structure. Fig. 5c,d, deposited at 580°C and 10 mtorr by ILPCVD, show some elliptic crystallites of BIC near the film/substrate interface rather than crystallite layer. Fig. 6a corresponds to the mixed-phase film of (311)-texture, as seen in Fig. 2a, for a pressure of 2.7 mtorr, for 560°C ILPCVD. Fig. 6b corresponds to mixed-phase film of intermediate texture preference between (311) and (111), as shown in Fig. 2a, for a pressure of 4.6 mtorr, for 560°C ILPCVD. It shows surface-induced crystallites with an irregular
Fig. 6. XTEM bright field images for samples deposited at 560°C by ILPCVD at pressures (a) 2.7 mtorr, (b) 4.6 mtorr. Morphology of (a) is \(\langle 311 \rangle\) dominant mixed-phase, and that of (b) is intermediate between \(\langle 311 \rangle\) and \(\langle 111 \rangle\) preference where pre-existing \(\langle 311 \rangle\) preference and still weak, incubated \(\langle 111 \rangle\) preferred BIC coexist.

shape, and some bulk-induced elliptic crystallites. For \(\langle 311 \rangle\)-preferred mixed-phase films, the crystal growth rate was roughly obtained by the height of the crystallite layer in XTEM images divided by the time of growth, giving an activation energy of 3.1 eV, as shown in Fig. 7. The deposition rates or pressures were different for the cases of Fig. 4a, Fig. 5a, and Fig. 6a. The critical value of the surface diffusion length associated with the minimum deposition rate for the mixed-phase was independent of the particular set of deposition conditions [11]. Thus, just above that rate, the structural order of the amorphous silicon matrix dependent on the surface diffusion length was assumed to be nearly the same. It is also known that the process of structural relaxation needed to transform amorphous matrix to crystal phase is basically the same amongst a-Si(H) films prepared by various methods [20], and previously reported activation energy values for the growth rates obtained by experiments or simulations are 2.4–3.1 eV [15,20–22] in the same range as ours. Drosd and Washburn [22] showed a thermally activated event of moving the a/c interface by an atomistic model for the transformation of amorphous to crystalline silicon films. Masaki et al. [20] showed that the crystallite growth rate as a function of temperature was in an activated form and explained that it was due to an energy barrier height from the amorphous to crystalline state of 3.1 eV. Thus, our data confirmed the activated growth of the \(\langle 311 \rangle\)-preferred crystallite layer of the mixed-phase films at low deposition rates. However, in the case of higher deposition rates, \(\langle 311 \rangle\)-preferred growth was suppressed. In this case, columnar-like growth of crystallites is not generally observed (Fig. 4c, Fig. 5c, and Fig. 6b). As stated above, the columnar-like growth image of Fig. 4c in spite of the \(\langle 111 \rangle\)-preference was only due to the quick fill of an amorphous layer by BIC seeds crowded and fast in growth, compared to others at low deposition temperatures.

According to literature, as given in the introduction, it is commonly accepted that mixed-phase films have crystallites embedded in amorphous matrix and that
these embedded crystallites are formed at the initial deposition process and have \(\langle 311\rangle\)-preferred orientation. Their sizes and nucleation density become larger as deposition temperature increases or deposition pressure decreases. However, their thermal behaviors are different from author to author and the results are confusing. Most authors was interested in device-oriented research (the active layer of a solar cell, thin film transistor, etc.) and so worked only on very thin samples. Their thicknesses were smaller than the annealed final grain size, and thus, two-dimensional growth observations [11] were performed. The preferred orientation of the grains was affected by the thickness of films [18] and precise observation requires a thick and long-time deposited films. These observations were carried out and we found two new kinds of behaviors.

First, just above the minimum deposition rate for the mixed-phase, the initially deposited \(\langle 311\rangle\)-preferred crystallites grew with an activation energy of 3.1 eV, moving up the a/c interface. This surface-induced, moving interface preserved the \(\langle 111\rangle\)-preference during deposition (Fig. 3a). This meant that regrowth by SIC did not change the preferred orientation even if large elliptic grains of \(\langle 111\rangle\)-preferred crystallites started to show up by BIC. In this situation, the nucleation density was high enough to create a crystallite layer composed of crowded \(\langle 311\rangle\)-preferred crystallites. This situation prefers a somewhat columnar-like growth [18] (Fig. 4a, Fig. 5a, and Fig. 6a) but real columnar growth leading to \(\langle 110\rangle\) polysilicon growth demands further increased nucleation. We called this a quasi-columnar growth. In this case, the \(\langle 110\rangle\) columnar growth was disrupted and replaced by other preferences. Among these, the \(\langle 100\rangle\) preference was quickly extinguished [23], while \(\langle 311\rangle\) and \(\langle 110\rangle\) preferences survived. The \(\langle 311\rangle\) preference was extinguished more easily than \(\langle 110\rangle\), but its regrowth rate was higher than that of \(\langle 110\rangle\) [24], compensating for its easy extinction. It seemed that this \(\langle 311\rangle\) preference could overtake the \(\langle 110\rangle\) preference at this quasi-columnar growth in our results. Once quasi-columnar growth begins, it cannot be overtaken by \(\langle 111\rangle\) preferred BIC because this requires incubation time. Secondly, as the deposition rate increased further, due to the small diffusion length of adatoms [11], the initially deposited \(\langle 311\rangle\)-preferred crystallites had a lower nucleation density and a smaller size, and thus they did not form a quasi-columnar growth. Soon this was overtaken by the conventionally incubated \(\langle 111\rangle\)-preferred elliptic BIC. A further increase of deposition rate resulted in no nucleation at the film/substrate interface, and pure amorphous silicon films were deposited. Bulk induced crystallization requires a long incubation time in amorphous silicon films.

4. Conclusion

We deposited polycrystalline films using 20% Si\(_2\)H\(_6\)/He gas by ILPCVD and LPCVD. We investigated the microstructural growth mechanisms of the mixed-phase silicon films using XRD and XTEM. There were two kinds of crystallites in the mixed-phase films. One was \(\langle 311\rangle\)-preferred small irregular crystallites occurring at the film/substrate interface in the initial deposition process. The other was conventionally incubated \(\langle 111\rangle\)-preferred bulk-induced crystallites. Depositions were performed for a long time compared to the incubation time of conventional BIC, and thick films were obtained in order to ensure a sufficient regrowth layer by SIC or BIC. We monitored the behavior of two kinds of crystallites and the following results were obtained.

At a given deposition temperature, a minimum deposition rate for the mixed-phase exists. Just above this deposition rate, the nucleation density and size of \(\langle 311\rangle\)-preferred crystallites are still large and this forms quasi-columnar growth where \(\langle 110\rangle\) columnar growth due to twin formation begins to be disrupted and allows the faster \(\langle 311\rangle\) growth. Initial \(\langle 311\rangle\) preference is preserved with this quasi-columnar growth with activation energy of 3.1 eV. As the deposition rate increases further, smaller nucleation density and crystallite size are insufficient for the quasi-columnar growth, and columnar regrowth of SIC is suppressed. Thus, conventional \(\langle 111\rangle\) preferred BIC overtakes them after an incubation time, because their elliptic growth rate is much faster. This results in a \(\langle 111\rangle\)-preferred mixed-phase with the small part of \(\langle 311\rangle\) preferred crystallites existing only near the film/substrate interface. Further increased deposition rate will result in purely amorphous silicon films with long incubation time.

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