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Nanocrystalline Si : H thin films grown at room temperature with plasma-enhanced chemical vapour deposition at a very high pressure

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Abstract
Hydrogenated nanocrystalline silicon (nc-Si : H) films were grown using the plasma-enhanced chemical vapour deposition method, with the plasma operated under a gas pressure of up to 30 mbar, i.e. on the verge of plasma instability. The heating effect in determining the crystallite size and crystalline volume fraction can be excluded as the maximum substrate temperature was below 80 °C at the end of growth. Crystallite initiation occurs in the plasma sheath, and Si nanocrystallites appear only when the gas pressure is above 10 mbar. With the pressure increasing to 30 mbar, the volume fraction of the nanocrystalline phase increases steadily, and the crystallite size changes from $\sim 7.8$ to $\sim 4.5$ nm. The optical bandgap of the deposits varies between 2.30 eV (at 15 mbar) and 2.03 eV (at 30 mbar), which can be explained in terms of the reduced hydrogen content and confinement effect. This work opens up the possibility of growing nc-Si : H films with well-controlled crystallite features on substrates held at near room temperature.

(Some figures may appear in colour only in the online journal)

1. Introduction
A hydrogenated amorphous silicon (a-Si : H) film is the fundamental material basis for many photovoltaic and microelectronic devices, and has been prepared using various distinct fabrication methods, in particular the plasma-enhanced chemical vapour deposition (PECVD) method, over the past few decades [1–3]. One critical reason for the vast application of a-Si : H thin films is the significantly reduced cost for the devices based on them, as for instance in the case of thin film solar cells in comparison with bulk Si solar cells, thus allowing large-scale implementation of these devices. With the PECVD method, hydrogenated silicon films of a widely variable bandgap can be conveniently obtained through the adjustment of deposition parameters, since the microstructure, including the content of H, of the deposits depends critically on the growth condition.

Under appropriate growth conditions, hydrogenated nanocrystalline Si (nc-Si : H) films comprising tiny Si crystallites embedded in the amorphous matrix could also be obtained. The optical bandgap of the nc-Si : H films can differ significantly from that of the amorphous ones [4]. For nc-Si : H films with a large crystallite size and a high volume fraction of the crystalline phase (>50%), the optical bandgap can be as small as less than 1.4 eV so that they have been structured as the base layer to absorb low-energy photons in a tandem solar cell design [5, 6]. In those nc-Si : H films containing Si crystallites of size down to 3–6 nm, the quantum confinement effect comes into play so that the optical bandgap can be widened to be larger than that of a-Si : H, thus they could be used as the top layer to reduce the thermalization effect arising from absorption of high-energy photons or as p-type window layer, resulting in an increased light transmittance for the cells [7, 8]. Moreover, an nc-Si : H film is also more stable
against photoinduced degradation, which is mainly induced by the S–W effect [9, 10]. Other features of merit of nc-Si: H films include low electronic defect density, high mobility of photogenerated current carriers, etc [11].

nc-Si: H films are usually fabricated, using PECVD, at a substrate temperature in the range 150–300 °C. In this circumstance, heating of the substrates is always a necessary step [12–14]. There is a strong practical motivation to fabricate nc-Si: H thin films on cold substrates. In recent years, there have been many reports on the growth of nc-Si: H thin films onto substrates at low temperatures or even at room temperature [15–17], where often tricks such as adding helium to the plasma [15] or applying an ac bias [16] to facilitate the nucleation of nanocrystallites are adopted. As plasma heating may eventually raise the substrate temperature, the features of nanocrystalline phase often depend on the film growth process.

Based on our previous work on the growth of various Si nanostructures with PECVD, it has been demonstrated that silicon compound films with Si nanocrystallites of well-controlled size can be grown onto glass and Si wafers without any intentional heating of the substrates [18–21]. There the nucleation of silicon particles occurs in the plasma sheath rather than in the growing film, hence the crystallite size and the volume fraction of the crystalline phase can be partially decoupled from the film growth process [18]. The success of the procedure depends critically on the working pressure, rather than the power supply or the dilution ratio of silane by hydrogen. It is conceivable that for the growth of nc-Si: H films, a much higher working gas pressure is desirable than that for growing a-Si: H films, which, however, may bring some problems with the operation of the plasma since beyond a threshold gas pressure the plasma will become unstable and non-homogeneous. It is of practical importance to establish the correspondence between the film properties and the working parameters for the growth of nc-Si: H films, where a very high pressure is employed, which can help one to optimize the implementation of nc-Si: H films in devices.

In this paper we report the growth of nc-Si: H thin films using the PECVD method without intentional heating of the substrate, for which the gas pressure is adjusted up to 30 mbar—the upper limit to maintain a stable and homogeneous glow discharge under other given conditions. The crystallites begin to appear at a threshold pressure, and at even higher gas pressures the crystallites become smaller while the volume fraction of the nanocrystalline phase increases. The influence of plasma conditions on the structural and chemical properties, consequently on the optical bandgap, of the deposits was discussed based on characterization results.

2. Experiment

Hydrogenated amorphous and nanocrystalline silicon films were grown on silica glass and c-Si wafer substrates using a custom-designed capacitively coupled PECVD system operated at 27.12 MHz, for which a conventional parallel-plate geometry was adopted. The electrode separation was 20 mm. The working gas was SiH4 diluted with H2 at a volume ratio of 1 : 100, which was introduced into the reaction chamber through the low-lying active electrode with regularly arranged holes (ϕ = 2 mm). The substrates were fixed on the ground electrode, thus the contamination from plasma dusts, which are usually present under very high pressure and high power conditions, could be avoided. For the growth of the samples under study, the total flow rate of the working gas was maintained at 20 sccm, and the gas pressure, monitored by a capacitance gauge (Pfeiffer CMR362), was set at values between 2.5 and 30 mbar by adjusting the pumping rate. Since no intentional heating of the substrate was applied, the substrate temperature at the end of growth experienced, with the power supply fixed at 50 W, an increment ranging from 30 to 50 °C depending on the gas pressure.

For all given conditions, the films were deposited onto both quartz glass and c-Si wafer substrates; those deposits on the c-Si wafer were used for Fourier-transform infrared measurements, and Raman spectra and transmittance were measured on those grown on quartz glass. The crystallinity of the deposits was evaluated on the basis of Raman spectra, which were obtained using the 532 nm line from a semiconductor laser (Horiba JY HR800). To avoid laser-induced crystallization, the power of the excitation source was kept under 1 mW. Fourier-transform infrared spectra (Bio-Rad, FTS-60V) were recorded to determine the Si–H bonding features of the deposits. The transmittance in the UV–visible range was measured with a transmittance spectrometer (Princeton instruments SP2500i), and the film thickness was determined using a Talystep profilometer (Veeco Dektak 8).

3. Results and discussion

3.1. Structural features

Raman spectroscopy is a very effective tool for the evaluation of crystallinity of silicon deposits. The shift with respect to 521.6 cm⁻¹ referred to the TO mode of single-crystalline Si, of which the full-width at half-maximum is 5.0 cm⁻¹ (measured here with the same spectrometer), is quite sensitive to the variation of phonon density of states, and consequently to the crystallinity of the deposits. In an amorphous Si sample, the Raman peak becomes broadened and downshifts to be centred at ~480 cm⁻¹. Thus, the profile features of the Raman peak, including the width and its position between 480 and 521.6 cm⁻¹, can be used to evaluate the crystallinity of the deposits, i.e. to infer the averaged crystallite size and volume fraction of the crystalline phase in the deposit [22]. The Raman peak arising from the TO mode of a nc-Si: H film can be resolved into three components: Ic not far from 521 cm⁻¹ for the crystalline fraction, Ia around 480 cm⁻¹ for the amorphous phase and Im around 510 cm⁻¹ to account for the effect of crystalline domain [23, 24]. The volume fraction of the crystalline phase, Xc, can be roughly estimated using the relation Xc = (Ic + Im) / (Ic + Im + Ia). At the same time, the averaged crystallite size, d in nm, can be obtained from the formula d = 2πBΔω / Δω, where Δω is the peak shift for the nanocrystalline component from that of a single-crystalline Si sample, and B = 2.0 cm⁻¹ nm² taken from [24, 25].
Figure 1. Raman spectra of the Si:H films deposited at gas pressures of 2.5, 5.0, 10, 15 and 30 mbar; RF power: 50 W.

Figure 2. Deposition rate as a function of gas pressure for the Si:H films, showing a distinct structure-related dependence.

Figure 1 displays the Raman spectra of the Si:H films grown under gas pressures of 2.5, 5.0, 10, 15 and 30.0 mbar. It can be seen that for the samples obtained with low gas pressures, i.e. 2.5 and 5.0 mbar, the Raman spectra exhibit only a broad peak centred at \( \sim 480 \text{ cm}^{-1} \), indicating that the deposits are typical a-Si:H films. At 7.5 mbar (not shown), another distinct peak begins to emerge at \( \sim 516.4 \text{ cm}^{-1} \) on the broad background for the amorphous phase. As the gas pressure is raised to 10 mbar, we see that the peak, now shifted to 520.3 cm\(^{-1}\), becomes quite prominent, and the half-width measures only \( \sim 17 \text{ cm}^{-1} \). It can be said with confidence that the deposit now contains some Si nanocrystallites. According to the peak shift \( \Delta \omega \) from 521.6 cm\(^{-1}\), the averaged crystallite size, \( d \), is estimated to be \( \sim 7.8 \) nm. With a further increase in pressure the peak becomes more intensive, and it shifts continually down to 518.1 cm\(^{-1}\) (half-width 15.2 cm\(^{-1}\)) at 15 mbar, and to 517.7 cm\(^{-1}\) at 30.0 mbar (half-width 11.8 cm\(^{-1}\)), corresponding to an averaged crystallite size of 4.7 nm and 4.5 nm, respectively. Clearly, the higher gas pressure facilitates the formation of crystalline parts in the deposits, and at 30.0 mbar the volume fraction of crystallites amounts to over 65\%, as roughly estimated from the peak decomposition. The pressure of 10.0 mbar could be safely taken as the threshold gas pressure, with other parameters given for the current setup, for the growth to result in nc-Si:H instead of a-Si:H films.

For these Si:H films grown by PECVD, the deposition rate is determined by gas pressure, as shown in figure 2, in a way relevant to the structural nature of the deposits. In the pressure range from 2.5 to 10 mbar, where the growth is dominated by a-Si:H deposition, the growth rate decreases slightly with increasing pressure—it changes from 0.12 nm s\(^{-1}\) at 2.5 mbar, through 0.08 at 5.0 mbar, down to 0.07 nm s\(^{-1}\) at 10.0 mbar. When it comes into the domain of nc-Si:H growth, a steady increase in the growth rate is observed, so that it jumps to a value as high as 0.42 nm s\(^{-1}\) at 30.0 mbar through 0.18 nm s\(^{-1}\) for 15 mbar and 0.31 nm s\(^{-1}\) for 20 mbar. This can be understood on the basis of the fact that growth of Si:H films in a hydrogen plasma involves a competition between the deposition of precursor particles and the etching process by atomic H [26]. Atomic H in the plasma can break the weak Si–Si bonds and etch them away, thus being an unfavourable factor for deposition. In the earlier stage of gas pressure increase, it leads to a more effective etching rather than to enhance the deposition, since the most remarkable change of dissociation products in the plasma is the overwhelming augmentation of atomic H species instead of Si–H radicals, remembering that the SiH\(_4\) content in the gas mixture is only 1.0 vol\%. Another effect of the increased density of atomic H is to saturate the dangling bonds of Si atoms on the surface, together with local bombardment through H impact on the growth front. The momentum transfer to the growth front from the H atoms will foster the diffusion of Si–H radicals on the surface, to be incorporated at sites where a rigid configuration with more Si–Si bonds is present, thus promoting the formation of nanocrystallites. For the formation of a nc-Si:H film, the kinetic energy of silyl radicals (especially SiH\(_3\)) adsorbed on the surface has to be sufficiently large so as to be able to diffuse towards and become combined at the energetically favourable sites responsible for nucleation and growth of nanocrystallites [27–29].

The generation of high-density atomic hydrogen in the plasma is a crucial factor for the growth of crystalline Si films at low temperatures. For the conventional growth of nc-Si:H films by PECVD at below 0.1 mbar, substrate heating to over 150 °C is usually needed. With the high-pressure condition in this work, the density of atomic hydrogen in the plasma probably suffices to promote crystallization, resulting in the growth of nc-Si:H films at room temperature without additional heating. With the high gas pressure, more silyl radicals are available to promote the growth process, which also leads to a larger deposition rate.

Generally, the nc-Si:H film growth mode can be described as follows: a totally amorphous Si:H thin layer (a few tens of nm) was initiated immediately onto the substrate, in which nucleation may occur at some places and these nuclei grow to nanocrystallites. In the subsequent stage, the film continues to grow into a mixed phase [27]. This is why thickness
dependence of film crystallinity was observed [17]. In our case, nucleation events are dominantly initiated by tiny particles from the plasma, which occur more frequently in a high-pressure plasma of silane and hydrogen [18]. For the two a-Si : H samples deposited at 2.5 mbar, one for 0.5 h (∼205 nm thick) and the other for 1.5 h (∼610 nm thick), the Raman spectra exhibit no noticeable difference, displaying only a pronounced feature around 480 cm⁻¹ (figure 3(a)). This is to say that the Si : H deposits remain amorphous throughout the growth process with the film thickness extending to 600 nm. No initialization of crystallite growth is identifiable in this case.

In order to investigate the growth process of nc-Si : H films under high-pressure conditions, a series of samples were deposited at 30.0 mbar for time durations of 5, 15 and 30 min. The corresponding Raman spectra of the TO phonon mode for these three samples (figure 3(b)) reveal the transition of the deposits with increasing nc-Si fraction—the longer the growth time, thus the thicker the sample, the more the nc-Si component in the deposit. This reminds us that the nc-Si : H growth proceeds here with the modification and enlargement of nuclei from the plasma [20].

3.2. Chemical features

The electrical and optical properties of the a-Si : H film are strongly affected by the silicon–hydrogen bonding configuration and its content. For the characterization of the chemical features of Si : H deposits, FTIR spectra recorded in the transmission mode are presented in figure 4. These spectra are normalized with regard to the film thickness, and offset vertically for clarity. From the site and intensity of the various absorption bands, the silicon–hydrogen bonding configuration can be inferred. As seen from figure 4, the deposits usually manifest some major absorption bands at ∼630, 700–1000, 1100 and 2100 cm⁻¹. The IR absorption for a-Si : H and nc-Si : H films has been extensively investigated, and assignment of the absorption bands to a particular Si–H bond configuration has been well established. Namely, the two absorption bands at 630 cm⁻¹ and 2000 cm⁻¹ are attributed to the rocking/wagging mode and stretching mode of the mono-hydrogen bond (Si–H), respectively [30, 31]. The peaks ranging over 700–1000 cm⁻¹, especially the two minor peaks centred at 840 and 890 cm⁻¹, correspond to the stretching/bending modes of the di-hydride (Si–H₂) and poly-hydride ((Si–H₂)₂) complexes. Moreover, the peak at 2100 cm⁻¹ corresponds to the stretching mode of Si–H₂, which can be blurred by (Si–H₂)n, SiH₃ radicals into a broad absorption band [32]. In addition to the features arising from the various silicon–hydrogen bond configurations, these deposits also show an absorption peak at 1000–1200 cm⁻¹, which is related to the Si–O stretching mode [33], caused by the exposure of the sample to the ambient.

As these spectra are normalized with regard to the film thickness, the content of different silicon–hydrogen bonding configurations could be compared to investigate the effect of gas pressure on the bonding status of Si : H film deposits. The incorporated H content could be conventionally estimated from the wagging mode on the IR absorption spectrum [34]. As seen from the FTIR spectra, all the absorption bands become weakened with increasing gas pressure, indicating a reduced hydrogen content in the deposit. In particular, the
Si–H₂-related vibrational modes decrease more significantly. In the a-Si : H films obtained at low pressures, only the content of Si–H₂ bonds shows a remarkable decrease, while the content of Si–H bond changes only slightly.

In photoelectric applications of Si : H films, the photoinduced degradation due to the creation of dangling bonds from the Si–H₂ structure is the key factor restricting the efficiency. It has long been recognized that low substrate temperature and high deposition rate lead to a large Si–H₂ density in deposits [9]. In this study, it is also shown that the growth rate of the a-Si: H film deposited at 2.5 mbar was higher than that deposited at 5.0 mbar (see figure 2), hence a higher Si–H₂ density. This means that for the growth at near room temperature, the photoelectric property of the a-Si: H films deposited under the higher pressure condition may be relatively better, especially when degradation is of concern.

As growth shifts from the a-Si : H domain into the nc-Si : H domain, the H content in the film decreases, and a large number of Si atoms combine more neatly to exclude hydrogen. Even at temperatures only slightly over room temperature (<80 °C), the high gas pressure condition yields nc-Si : H films that are more resistive to photoinduced degradation. The appearance of the absorption band at 1000–1200 cm⁻¹ assigned to the Si–O mode indicates the oxidation effect caused by the porous-like microsturcture of the deposits. As the deposition pressure increases, the intensity of this Si–O mode obviously decreases, implying that the high pressure would have given rise to a more compact deposit structure.

3.3. Optical features

The transmittance spectra of the Si : H deposits at shorter wavelengths, below 550 nm or so as shown in figure 5(a), can be used to infer the optical bandgap. Because of the uniform thickness of the films, coherent multiple reflection invoked some interference fringes on the spectra. In the part of shorter wavelengths, where the transmittance is rather small, the interference effect would be almost completely suppressed so that the transmittance shows a smooth curve that rises monotonically with increasing wavelength. In this region, the transmittance curve is exclusively the result of band-edge absorption, therefore the absorption coefficient of the deposits around the absorption edge can be calculated from the measured transmittance. Figure 5(b) displays the √αhv versus hv curves for the samples, which, except for the first few data points, exhibit a quite satisfactory linearity. From the Tauc relation √αhv = B(hv − Eg) [35], the optical bandgap can be determined. For the two amorphous samples, the optical bandgap thus obtained remains unchanged within the accuracy of the method; it is 2.13 eV. For the sample obtained at 7.5 mbar, wherein some nanocrystallites are present, the optical bandgap is 2.295 eV. It then goes through 2.25 eV for the 10 mbar sample to reach the maximum value of 2.30 eV for the 15 mbar sample, and thereafter it drops. For the sample deposited at 20 mbar it is 2.18 eV (not shown in figure 5) and for that at 30 mbar it drops abruptly to 2.03 eV, even 0.1 eV smaller than the amorphous ones. The fluctuation of the bandgap value reflects the change in the deposit microstructure with the varied deposition conditions.

Figure 5. (a) Transmittance spectra and (b) plot of (αhv)¹/² versus hv of the Si : H films deposited at different pressures.

In the a-Si : H films, the optical bandgap is known to depend on the hydrogen content, which can be calculated from the wagging mode as it increases nearly in proportion to the hydrogen content [36]. As shown in figure 2, the hydrogen content of the samples deposited at 2.5 and 5.0 mbar, as revealed by the wagging mode at 630 cm⁻¹, is nearly the same, thus it is reasonable that these two films have the same optical bandgap. For nc-Si : H samples, the optical bandgap is not only a function of the hydrogen content, but is also influenced by the nc-Si particles embedded in the amorphous matrix. The nc-Si crystallites smaller than 10 nm manifest a quantum confinement effect, which leads to the widening of the bandgap. The fact that the optical bandgap of the nc-Si : H films obtained at 7.5–20 mbar is larger than that of the a-Si : H samples originates from the confinement effect of nc-Si particles. In the film deposited at 30.0 mbar, the reduced optical bandgap may be attributed to the effect of serious hydrogen loss—the decreased hydrogen content may eventually outbalance the quantum confinement effect.

4. Conclusion

Nc-Si : H films were grown on cold substrates, with the substrate temperature remaining below 80 °C at the end of
growth, using PECVD operated under high gas pressures. The effect of gas pressure, and consequently of the plasma condition, on the structural and optical features of the deposited Si:H films was investigated. As nucleation occurs in the plasma sheath, a gas pressure over a threshold value, here \( \sim 10 \text{ mbar} \), has to be applied to obtain nc-Si:H deposits. The volume fraction of the nanocrystalline phase increases with increasing gas pressure so that at 30 mbar it reaches over 65%. At the same time, the Si–H bond characteristic of the amorphous samples become less. Silicon crystallization at nearly room temperature could be attributed to the high-density atomic hydrogen in the plasma. The optical bandgap of the nanocrystalline samples varies in the range from 2.30 to 2.03 eV, which can be explained in terms of the Si–H content and quantum confinement effect. This work demonstrates that nc-Si:H films can be grown simply with PECVD operated at high pressures onto substrates held at near room temperature.

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