Section 11. Growth and structure

Influence of hydrogen on the structural order of microcrystalline silicon during the growth process

I. Beckers a,*, N.H. Nickel a, W. Pilz b, W. Fuhs a

a Hahn-Meitner Institut Berlin, Rudower Chaussee 5, 12489 Berlin, Germany
b Bundesanstalt für Materialforschung und-prüfung, Unter den Eichen 78, 12205 Berlin, Germany

Abstract

Commonly, the transition of amorphous to microcrystalline growth is achieved by diluting silane (SiH4) with hydrogen (H2). Increasing hydrogen dilution causes an increase of crystallinity. However, at high H dilution ($\Delta H > 0.98$), the crystallinity is found to decrease after reaching a maximum. A decrease of crystallinity is also observed in microcrystalline silicon ($\mu$-c-Si) samples after a post-hydrogenation treatment. These experiments show that hydrogen incorporation into the structure leads to loss in the structural order due to an H-induced conversion of Si–Si bonds into strained or weak Si–Si bonds. The implications of these results for the growth mechanisms are discussed.

Keywords: Hydrogen; Microcrystalline silicon; ECRCVD

1. Introduction

Commonly, in plasma-enhanced chemical vapor deposition (PECVD) techniques, the transition from the amorphous to the microcrystalline phase is achieved by hydrogen dilution of silane (SiH4) because of an enhanced surface mobility [1]. Another process which may be responsible for this phase transition is hydrogen (H2) etching of the disordered phase during the growth process [2]. Moreover, hydrogen controls the structure, defect concentration, electrical properties, and growth mechanism of microcrystalline-silicon ($\mu$-c-Si) films by eliminating unfavorable configurations such as weak or strained Si–Si bonds, and H is known to assist in bonding reconstruction in a subsurface layer [3]. With increasing hydrogen dilution, the crystallinity of $\mu$-c-Si films increases to a maximum and then decreases [4,5]. In this paper, the effects of hydrogen on the structural properties of $\mu$-c-Si is investigated in more detail. We show that the decrease of the crystallinity, $X_c$, at high H-dilution is due to hydrogen-mediated conversion of Si–Si bonds into strained or weak Si–Si bonds.

2. Experiments

Electron cyclotron resonance chemical vapor deposition (ECRCVD) has been used to prepare $\mu$-c-Si films with a deposition time of 1800 s at 325°C using hydrogen as excitation gas. Silane decomposition occurs downstream from the plasma, by impact, with the ionized excitation gas. Hydrogen dilution is
accomplished either with the excitation gas or by mixing silane with hydrogen before entering the deposition chamber. The plasma is ignited using a microwave frequency of 2.45 GHz, a microwave power of 1000 W, and a magnetic field of 8.1875 T. Some \( \mu c \)-Si samples were post-hydrogenated at 325°C with a microwave power of either 100 or 1000 W.

Step-profiling was used to determine the deposition rate of each sample. Hydrogen concentrations were measured using secondary-ion mass spectrometry (SIMS), and the crystallinity was obtained from Raman backscattering measurements.

3. Results

The crystalline fraction, \( X_c \), of \( \mu c \)-Si films was estimated from the integrated Raman intensities [6,7]. The peak, in the range of 510 cm\(^{-1}\), is commonly attributed to an intermediate phase at grain boundaries [7,8]. The crystalline fraction as a function of hydrogen dilution, \( \Delta H = [H_2]/([H_2]+[SiH_4]) \), is shown by the solid symbols in Fig. 1. The crystallinity of \( \mu c \)-Si films prepared at a given H dilution was not dependent on the film thickness. At low hydrogen dilution (\( \Delta H < 0.9 \)), the samples are amorphous. Crystallinity is obtained for hydrogen dilution, \( \Delta H > 0.9 \). The crystalline fraction increases monotonically with increasing \( \Delta H \) and exhibits a maximum at \( \Delta H = 0.98 \). A further increase of \( \Delta H \) results in a decrease of the crystalline fraction. For this set of samples, hydrogen dilution was accomplished via the excitation gas. When increasing the hydrogen dilution by adding H directly to silane, the crystalline fraction increases further to a new maximum and then decreases (solid circles in Fig. 1).

This change is due to an increase in the deposition pressure [4].

The crystalline fraction as a function of the deposition rate, \( R_d \), is depicted by the open symbols in Fig. 1. With increasing crystalline fraction, the deposition rate decreases from \( \approx 1.7 \) nm/s at \( X_c = 0\% \) to \( \approx 0.1 \) nm/s at \( X_c = 94\% \). This decrease is consistent with common growth models [1–3,9,10]. Moreover, an etching rate of \( \approx 0.02 \) nm/s was obtained when single-crystal silicon was exposed to a pure hydrogen plasma at a microwave power of 1000 W. It is interesting to note that the deposition rate and the crystallinity increase for \( \Delta H > 0.99 \) when \( H_2 \) and \( SiH_4 \) are mixed (open circles).

![Fig. 1. Crystallinity, \( X_c \), as a function of the hydrogen dilution, \( \Delta H \), (solid symbols and bottom axis) and the deposition rate, \( R_d \), (open symbols and top axis). Details are described in the text. The lines are a guide to the eye.](image1)

![Fig. 2. Hydrogen concentration as a function of the crystalline fraction of the microcrystalline silicon films. The line is a guide to the eye.](image2)
Fig. 2 shows the hydrogen concentration, $C_H$, as a function of the crystalline fraction. We find an average H concentration of $\approx 6.5$ at.% independent of $X_c$, indicating that the chemical potential of hydrogen is pinned. This H concentration is large, considering the fact that microcrystalline silicon generally contains about 1 to 3 at.% hydrogen [11].

Further information on the effect of H on the structural properties of $\mu$-c-Si was obtained from post-hydrogenation experiments. Three samples were exposed to a pure hydrogen plasma for 60 min, and subsequently, the crystalline fraction was determined again. In Fig. 3, the crystalline fraction of the post-hydrogenated samples is plotted vs. $X_c$ of the as-deposited specimens. All $\mu$-c-Si samples reveal a decrease in crystallinity due to the post-hydrogenation treatment. Moreover, the H-induced decrease of $X_c$ is larger in samples with an initially longer crystalline fraction. This increase is indicated by the dashed line (slope $\leq 1$).

Fig. 4 shows Raman spectra of single-crystal silicon after 3 min and 80 min at a plasma power of 100 W. In contrast to results reported previously [12], the Raman spectra do not indicate the formation of an amorphous phase. However, according to transmission electron microscopy (TEM) micrographs, the introduction of hydrogen into the samples resulted in the formation of hydrogen-stabilized platelets (see inset in Fig. 4). Platelets are structural defects predominantly oriented along $\{111\}$ crystallographic planes [13,14].

4. Discussion

The experimental results presented above have a number of important implications. The decrease of the crystalline fraction in the higher dilution range ($\Delta_D > 98\%$) cannot be explained by common growth processes [4]. With increasing H dilution, surface models [1,2] and growth zone models [3,9,10] predict an increase of $X_c$. Thus, an additional process is required to explain the decrease in $X_c$ in the high dilution range with increasing $\Delta_D$. One explanation for this behavior could be an increase of the lattice strain caused by the incorporation of oxygen into the silicon network. The oxygen concentration is expected to increase with decreasing deposition rate and hence, the crystallinity should depend on $R_d$. 

---

Fig. 3. The crystallinity after post-hydrogenation treatment vs. the initial crystalline fraction. The specimens were exposed to an ECR hydrogen-plasma at 320°C and 1000 W for 60 min. The dashed line is a least squares fit to the data.

Fig. 4. Raman spectra measured on c-Si after post-hydrogenation at 100 W for (a) 3 min and (b) 60 min. The TEM micrograph in the inset shows a hydrogen-stabilized platelet obtained after an exposure to H for 3 min at 100 W.
However, this is not the case, since in the extremely high dilution range ($\Delta_H > 98\%$), the deposition rate increases with increasing $\Delta_H$. A similar behavior has been found at different $\Delta_H$ when varying the pressure [4].

During the growth process, the distribution of H in the film is determined by the chemical potential of hydrogen, $\mu_H$. Adding more H to the reactant gas results in an increase of $\mu_H$, and hence causes a further reduction of the amorphous phase [3]. In our case, however, the H concentration in the deposited films is approximately independent of the crystallinity and hence, of the hydrogen dilution (Fig. 2), indicating that $\mu_H$ is pinned. From SIMS measurements, the effective diffusion-coefficient for H out-diffusion was estimated to be $D_{eff} = 6 \times 10^{-14}$ cm$^2$/s at 460°C. With this information, the position of $\mu_H$ can be determined using the relation [15]:

$$E_M - \mu_H(T) = -kT \ln \left( \frac{D_{eff}}{D_0} \right),$$

where $E_M$ is the migration saddle-point for H migration, and the microscopic diffusion pre-factor is given by $D_0 = 1/6\nu a^2$, where $\nu$ is the attempt frequency and $a$ is the mean free path. With reasonable assumptions of $a \approx 0.3$ nm and $\nu \approx 10^{12}$ Hz, $D_0$ amounts to $10^{-3}$ cm$^2$/s. Thus, at 460 K, $\mu_H$ is pinned at $E_M - \mu_H = 1.5$ eV. This value is smaller than in amorphous silicon (1.5 to 2 eV) [15] and about 0.2 eV larger than in poly-Si with a comparable hydrogen concentration [16].

According to SIMS measurements, post-hydrogenation for 60 min at 365°C results in an increase of the total H concentration in the near surface region. However, the increase of the H content is a small fraction of the amount already present and therefore, the position of $\mu_H$ remains essentially unchanged. On the other hand, a decrease of the crystallinity could be due to plasma damage. However, this is not the case, since post-hydrogenation of c-Si for up to 80 min did not result in the formation of an amorphous phase, but generated hydrogen-stabilized platelets (Fig. 4). The fact that Raman measurements do not indicate the presence of an amorphous phase in post-hydrogenated c-Si samples could also be due to an inability to detect the bands, or a concentration of the amorphous phase that is a small fraction of the c-Si phase.

Thus, our data indicate that the decrease of crystallinity at higher H dilution indicates the presence of a hitherto unexpected property of hydrogen namely, the ability of H to transform crystalline silicon into amorphous silicon. The lack of an amorphous phase in post-hydrogenated c-Si indicates that the hydrogen-mediated conversion of c-Si into a-Si occurs at grain boundaries; the presence of lattice strain decreases the formation energy of the amorphous phase. This decrease is consistent with previous results obtained on amorphous silicon that showed that internal strain propagates within the network and can be generated or reduced by incorporation or annealing of hydrogen [17].

5. Conclusions

Microcrystalline silicon films have been prepared using silane diluted with hydrogen. At a dilution of $\Delta_H = 0.98$, a maximum in crystallinity is observed. At higher H dilution, the crystallinity decreases. Post-hydrogenation treatments of $\mu c$-Si samples also result in a decrease of the crystalline fraction. On the other hand, a similar treatment performed on c-Si did not produce an amorphous phase, however, hydrogenation caused the formation of H-stabilized platelets. These results suggest that the decrease in crystallinity is due to the hydrogen-induced transformation of strong Si–Si bonds into weak Si–Si bonds which is promoted by the presence of strain at grain boundaries.

Acknowledgements

This work was supported by the Bundesministerium für Bildung und Forschung BMBF.

References


