RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 58, NUMBER 4 15 JULY 1998-II

Hydrogen-mediated structural changes of amorphous and microcrystalline silicon

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(Received 26 March 1998; revised manuscript received 12 May 1998)

Amorphous (a-Si:H) and microcrystalline silicon (μc-Si:H) samples were exposed to a hydrogen plasma in a clean electron-cyclotron-resonance system. We present unequivocal experimental evidence for hydrogen-induced crystallization of a-Si:H. A 60-min post-hydrogenation at 325 °C resulted in an increase of the crystalline fraction by 10–15 %. Similar H plasma treatments performed on μc-Si:H caused a decrease of the crystalline fraction X_C by up to 20%. The lack of an amorphous phase in posthydrogenated c-Si shows that the presence of grain boundaries is required to observe hydrogen-induced conversion of crystalline to amorphous silicon. We propose that the driving force for the decrease of X_C is the minimization of the lattice-strain energy. [S0163-1829(98)50928-9]

Usually, the growth of hydrogenated microcrystalline silicon (μc-Si:H) is achieved either by hydrogen dilution of silane[1] or by the layer-by-layer deposition technique.[2] In the latter technique, hydrogenated amorphous silicon (a-Si:H) deposition and hydrogen plasma treatments are carried out alternately. Until recently it was widely believed that a hydrogen plasma treatment of the a-Si:H layer caused structural rearrangements thereby leading to the formation of microcrystalline silicon.[2,3] However, Saitoh *et al.*[4] showed that microcrystalline growth using the layer-by-layer technique is due to chemical transport from the coated cathode to the substrate. Hydrogen etches the a-Si:H film on the cathode and thus produces silane related molecules and radicals leading to identical conditions for the growth of μc-Si:H as in case of high hydrogen dilution. On the other hand, using a clean cathode, the hydrogen plasma treatment resulted only in etching of the a-Si:H layer.[4]

In this paper we present unequivocal experimental evidence for hydrogen-induced crystallization of amorphous silicon. Hydrogen plasma treatments of a-Si:H for 60 min resulted in an increase of the crystalline fraction by 10 to 15%. On the other hand, similar H plasma treatments performed on hydrogenated microcrystalline silicon at a substrate temperature of 325 °C caused a pronounced decrease of the crystalline fraction by up to 20%. Moreover, our experimental results demonstrate that the latter transformation requires some degree of disorder as it is commonly found at grain boundaries.

Amorphous and microcrystalline silicon films were deposited in an electron-cyclotron-resonance chemical-vapor-deposition (ECRCVD) system. In order to achieve microcrystalline growth silane was diluted with 75 to 99.5% hydrogen. The microcrystalline silicon films were deposited at a substrate temperature of 325 °C and a pressure of 5 to 10 mTorr. The plasma was ignited using a microwave frequency of 2.45 GHz, a microwave power to 1000 W, and a magnetic field of 875 G. The average grain size was determined from cross-sectional transmission-electron-microscopy (TEM) micrographs and amounts to 150 Å for specimens with a crystalline fraction larger than 60%. Subsequently, the deposition system was cleaned and the specimens were exposed to a pure ECR hydrogen plasma at various temperatures for up to 2 h. Before and after each hydrogen plasma treatment the samples were characterized by Raman backscattering measurements performed at room temperature with a 632.8-nm laser line and a power of 15 mW. Also, the etching rate of the H plasma treatment was determined by measuring the change in thickness using a mechanical stylus.

The crystalline fraction X_C was obtained by the following procedure. The Raman spectra were fitted using three Gaussian curves with peaks at 480, 510, and 520 cm^{-1}. The peaks at 480 and 520 cm^{-1} represent the amorphous and the crystalline contributions to the Raman backscattering spectra, respectively, while the peak at 510 cm^{-1} is commonly attributed to the presence of tensile strained Si-Si bonds at grain boundaries.[5,6] X_C is given by the ratio of the integrated intensities of the Gaussian curves at 510 and 520 cm^{-1} to the total integrated intensity of the TO mode taking into account the ratio of the Raman backscattering cross sections of the crystalline to the amorphous contributions.[7] An increase (decrease) of X_C is due to either an increase (decrease) of the grain size or a decrease (increase) of the volume of the amorphous matrix.

In Fig. 1 the change of the crystalline fraction ΔX_C caused by posthydrogenation at 325 °C for 1 h is plotted as a function of the initial crystalline fraction X_C^{init}. The effect of the H plasma treatment depends strongly on the structural properties of the starting material. For hydrogenated amorphous silicon ($X_C^{\mathrm{init}} \approx 0$) an increase of the crystalline fraction of 10 to 15% is observed. Since vacuum anneals at substrate temperatures of 400 and 465 °C for 1 h did not result in an increase of the crystalline fraction, this result is an unequivocal experimental observation of a hydrogen-induced transformation from amorphous to microcrystalline silicon. On the other hand, the same plasma treatment performed on specimens with $X_C^{\mathrm{init}} > 30\%$ resulted in a pronounced decrease of X_C. The largest decrease of the crystalline fraction ($\Delta X_C = -20\%$) was observed in microcrystalline samples with $X_C^{\mathrm{init}} \approx 100\%$.

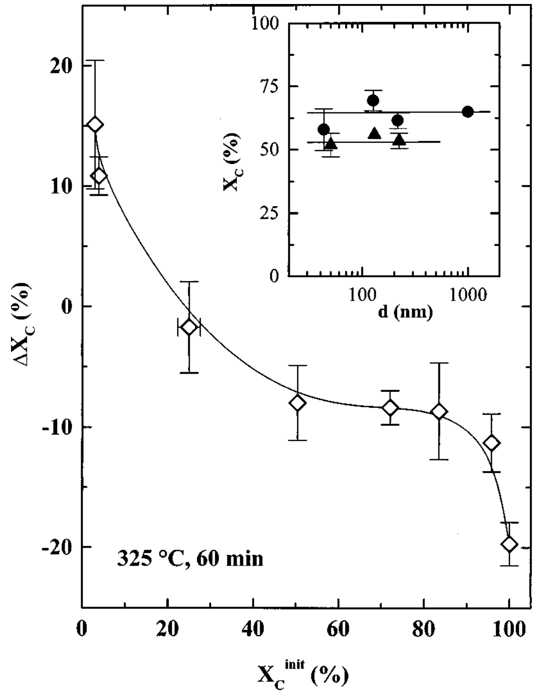

FIG. 1. Change of the crystalline fraction ΔX_C as a function of the initial crystalline fraction X_C^{init}, after posthydrogenation at 325 °C for 1 h. The influence of the sample thickness on the crystalline fraction is depicted in the inset. The triangles and circles represent two sets of samples deposited at 8 mTorr using a hydrogen dilution of 95 and 99%, respectively.

Hydrogen plasma treatments of silicon can result in significant etching of the specimens.[1,4] Since most preparation techniques produce μc-Si:H with an inhomogeneous distribution of the crystalline fraction with respect to the sample thickness, it is conceivable that the observed decrease of X_C is due to etching of the μc-Si:H specimens. Therefore, a series of μc-Si:H samples with a thickness varying between 0.05 to 1 μm was deposited and characterized by Raman measurements. The circles and triangles in the inset of Fig. 1 depict the dependence of X_C as a function of the sample thickness. The lack of a thickness dependence of X_C is characteristic for μc-Si:H deposited in an ECRCVD system. This result is corroborated by cross-sectional TEM micrographs revealing that microcrystalline growth starts at the interface. No evidence of an amorphous layer was found; this layer is commonly observed in specimens prepared by conventional plasma-enhanced chemical-vapor deposition (PECVD) techniques.[8]

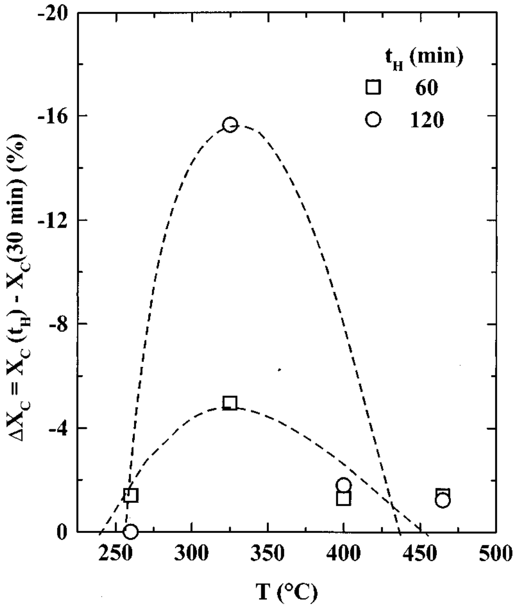

FIG. 2. Temperature dependence of the change in crystalline fraction. The squares and circles represent the change of X_C after hydrogen plasma treatments for 1 and 2 h with respect to X_C (30 min), respectively. The as-deposited specimens exhibited a crystalline fraction of $X_C = 72\%$.

The time and temperature dependence of the change of X_C was investigated using μc-Si:H samples with $X_C^{\text{init}} = 72\%$. Initially the sample surface is coated with a native oxide that imposes a barrier for H indiffusion.[9] Therefore, etching and structural changes of the microcrystalline samples will not occur instantaneously after the H plasma is ignited. Initially, the H plasma removes the native oxide, which can take several minutes depending on the oxide thickness. Since a new sample was used for each experiment, a better measure for the change of X_C is obtained when plotting the data with respect to the 30-min H plasma treatment. The squares and circles in Fig. 2 show the change of the crystalline fraction after a 1 and 2 h hydrogen plasma treatment at 325 °C with respect to X_C (30 min), respectively. Both sets of data indicate a maximum of ΔX_C at 325 °C and show a pronounced decrease at higher and lower substrate temperatures.

An important factor for understanding this behavior is the influence of the etching rate r_{etch}. The temperature dependence of the etching rate is plotted in Fig. 3. Analogous to the data shown in Fig. 2 the etching rate was determined from the decrease of the sample thickness between a 30- and 120-min hydrogen plasma treatment. With increasing substrate temperature r_{etch} decreases monotonically to values of approximately 0.07 Å/s at 465 °C. This suggests that at low

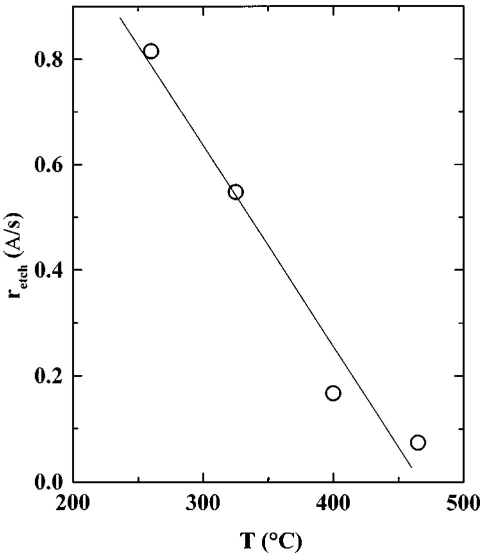

FIG. 3. Temperature dependence of the etching rate r_{etch}. The etching rate was determined from the decrease in sample thickness between a 30-min and a 120-min H plasma treatment.

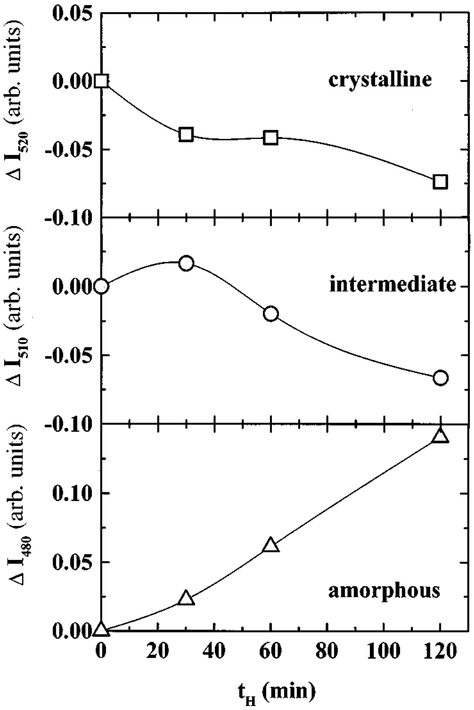

FIG. 4. Change of the integrated Raman intensities of the peaks at 480, 510, and 520 cm^{-1} vs hydrogenation time t_{H}. The data are normalized to the total integrated intensity of the TO mode. The hydrogen plasma exposures were performed at 325 °C. The as-deposited microcrystalline-silicon samples revealed a crystalline fraction of 72%.

temperatures the small decrease of X_C is due to enhanced etching of the specimens. Hydrogen-mediated structural changes advance from the surface and are diffusion limited. Thus, at low substrate temperatures the H-induced loss of the crystalline fraction occurs slowly because of a very small diffusion coefficient. Simultaneously, most of the structurally converted material is removed from the surface due to a high etching rate. Therefore, the measurable decrease of ΔX_C is small. With increasing temperature the H concentration in the specimen and in the plasma above the specimen decreases.[10] Secondary-ion-mass spectrometry measurements show a decrease of the H concentration that is more pronounced at higher temperatures. In addition, the hydrogen diffusion coefficient increases causing H to migrate more quickly into and out of the bulk. This leads to a decrease of the H concentration below a threshold value at which structural changes such as a decrease of X_C (Fig. 2) and etching (Fig. 3) occur.

In order to illuminate the origin of the hydrogen-mediated structural changes the Raman spectra were further analyzed by computing the time dependence of the integrated intensities of the crystalline, intermediate, and amorphous contributions. The change of the integrated intensities ΔI_{520}, ΔI_{510}, and ΔI_{480} versus the hydrogen exposure time t_{H} is plotted in Fig. 4. With increasing hydrogenation time, ΔI_{520} (crystalline contribution) decreases monotonically. The intensity of the intermediate peak, however, increases somewhat at short exposure times ($t_{\mathrm{H}}=30$ min) and then reveals a monotonic decrease. On the other hand, the integrated intensity of the peak at 480 cm^{-1} shows a pronounced increase indicating that the crystalline fraction of this specimen decreased. In contrast to previous reports,[11] similar H plasma treatments performed on single crystalline silicon did not result in the formation of an amorphous surface layer. However, H stabilized platelets were observed in cross-sectional TEM micrographs.[12] These results demonstrate that the presence of grain boundaries is required to observe a hydrogen-mediated decrease of the crystalline fraction in microcrystalline silicon.

The results shown in Figs. 1–4 have some important implications for the preparation of microcrystalline silicon. The recent report that a pure hydrogen plasma does not cause crystallization of a-Si:H (Ref. 4) is valid only for conventional rf power PECVD deposition systems. Our results in Fig. 1 clearly demonstrate that post-hydrogenation at moderate temperatures in a *clean* ECR system causes crystallization of a-Si:H. There are three different models explaining this effect: (i) The etching model suggests the formation of crystallites by a balance between deposition and etching on the growing surface;[1] (ii) the growth-zone model proposes structural relaxation of the amorphous phase followed by a transition to the crystalline phase in the subsurface region;[13] and (iii) the surface-reaction model suggests that the surface diffusivity of precursors is enhanced due to H termination of the surface.[14] The latter model cannot explain our results since the phase transition from amorphous to crystalline occurred in a post-hydrogen plasma treatment.

The hydrogen-induced phase transition depends strongly on the structural properties of the starting material. When the initial crystalline fraction X_C^{init} exceeds 20% the post hydrogenation treatment, causes an adverse effect, effectively reducing the crystalline fraction. Material with a small crystalline fraction is mainly composed of crystallites embedded in an amorphous matrix. For these samples the growth zone and the etching model predict a further increase of X_C. This, however, is not the case. The data in Fig. 1 clearly indicate the presence of an additional mechanism causing the decrease of the crystalline fraction. One possible explanation is plasma damage. However, according to cross-sectional TEM micrographs the plasma treatment did not introduce surface or subsurface damage in c-Si samples but generated hydrogen stabilized platelets.[12] The lack of an amorphous phase in post-hydrogenated c-Si indicates that for a H-induced conversion of crystalline to amorphous silicon, the presence of grain boundaries is required.

The analysis of the Raman spectra as a function of the hydrogenation time provides an important insight in the microscopic mechanism responsible for the decrease of the crystalline fraction in μc-Si:H (Fig. 4). In the first 30 min of the H plasma treatment the phase transformation from crystalline to grain-boundary material occurs concurrently with an increase of the amorphous phase. This indicates that the phase transformation originates at the grain boundaries.

A good measure for the average strain energy per network bond is the Urbach slope.[15] The Urbach energy for a-Si:H is about 50 meV. A good estimate of the strain energy at grain boundaries can be obtained from polycrystalline silicon (poly-Si) since it does not contain an amorphous phase. In hydrogen passivated poly-Si a typical value for the slope of the Urbach edge is 85 meV.[16] Thus, although the degree of disorder at grain boundaries is smaller than in amorphous silicon, since these two-dimensional interfaces reveal longrange order,[17] the average strain energy per network bond is roughly 35 meV larger at grain boundaries.

The introduction of hydrogen into μc-Si:H will cause a reduction of the strain energy at the grain boundaries by eliminating unfavorable bonding configurations such as strained Si-Si bonds. Once a steady state between strain annihilation and creation is reached a local reduction of strain will cause the generation of strain somewhere else in the lattice; the internal strain propagates within the network.[15] In the amorphous regions strain propagation will occur immediately. It is conceivable that this mechanism causes strain accumulation at the perimeter of crystallites leading to bond distortions of strong Si-Si bonds. The accumulated strain can then be reduced by inserting H atoms into strained Si-Si bonds causing the formation of Si-H and/or silicon dangling bonds. Eventually, this mechanism leads to an increase of disorder,[6] however, with a smaller average strain energy per network bond. In μc-Si:H with an amorphous matrix a large amount of strain can propagate within this matrix without ever reaching a grain. Thus, with decreasing volume of the amorphous tissue the amount of propagating strain ending up at the perimeter of a grain increases and therefore the decrease of X_C becomes more pronounced (Fig. 1). Hence, we propose that the driving force for the decrease of the crystalline fraction is the minimization of the lattice strain energy by migrating H atoms.

In summary, amorphous and microcrystalline silicon samples were exposed to a hydrogen plasma in a *clean* ECR system. We presented unequivocal experimental evidence for hydrogen-induced crystallization of a-Si:H. A 60-min post-hydrogenation at 325 °C resulted in an increase of the crystalline fraction by 10–15%. On the other hand, similar plasma treatments performed on samples with $X_C^{\text{init}} > 20\%$ caused a decrease of X_C. The largest decrease of $\approx 20\%$ was obtained at $X_C^{\text{init}} = 100\%$ and a hydrogenation temperature of 325 °C. At lower temperatures the dominant process is etching, while at higher temperatures ΔX_C decreases because of a decrease of the H concentration and enhanced H diffusivity. The lack of an amorphous phase in post-hydrogenated c-Si indicates that the presence of grain boundaries is required to observe H-induced conversion of crystalline to amorphous silicon. Based on the difference of the average strain energy in amorphous and polycrystalline silicon we propose that the driving force for the decrease of X_C is the minimization of the lattice strain energy by migrating H atoms. This is consistent with previous results obtained on amorphous silicon showing that internal strain propagates within the network and can be generated or reduced by migrating hydrogen.[15]

The authors are grateful to J. Krause for technical support. This work has been supported by the Bundesministerium für Bildung und Forschung, BMBF.

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