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Grain-boundary defects in laser-crystallized polycrystalline silicon

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Polycrystalline silicon (poly-Si) films were prepared by laser crystallization of amorphous silicon with various laser energy densities at substrate temperatures of 300 and 673 K. At $T_S = 300$ and 673 K poly-Si films with grain sizes of 1.5 and 1.0 μm were obtained at laser fluences of 540 and 505 mJ/cm^2, respectively. An increase of the grain size results in a decrease of the spin density due to a reduction of the grain-boundary volume. Moreover, the increase in substrate temperature resulted in a pronounced decrease of the spin density independent of the laser energy density. Defects are passivated by exposing the poly-Si films to monatomic H at 350 °C. This causes the spin density to decrease to a residual value of $\approx 9 \times 10^{16}$ cm^{-3} independent of substrate temperature and laser fluence. [S0163-1829(97)03444-9]

In the past, laser crystallization of amorphous silicon has been widely used to produce low-temperature polycrystalline silicon (poly-Si) thin-film transistors for large-area electronics.[1,2] As a function of laser fluence the morphology of the poly-Si films changes. At a very low laser fluence amorphous silicon is converted to a stratified system comprising an amorphous layer, a fine-grained poly-Si layer, and a large-grained layer.[3] At higher laser energy densities a small process window allows us to crystallize poly-Si with average grain sizes of more than 10 times the film thickness.[4,5] Melting and solidification processes as well as electrical properties of poly-Si films and devices have been studied intensively.[4–7] Information on the defect density is commonly obtained using the field-effect conductance method.[8,9] However, this method is indirect and cannot be applied to poly-Si films.

A direct method to measure grain-boundary defects is the electron paramagnetic resonance (EPR) technique, which has been used to identify these defects as silicon dangling-bonds.[10] In this paper we present a detailed investigation on the influence of laser-crystallization parameters on the silicon dangling-bond concentration. We find that poly-Si samples crystallized at room temperature reveal a considerably higher spin density, N_S, compared to specimens crystallized at elevated substrate temperatures. Independent of the substrate temperature, during laser crystallization the spin density decreases with increasing grain size. Model calculations of the spin density as a function of the grain size suggest that the decrease of N_S is not solely due to a decrease of the grain-boundary volume. Hydrogenation of the poly-Si films effectively passivates Si dangling bonds. Moreover, independent of substrate temperature and laser energy used for the crystallization N_S saturates at a residual value of $\approx 9 \times 10^{16}$ cm^{-3}.

Polycrystalline silicon films were fabricated in a two-step process. First, undoped amorphous silicon (a-Si) was deposited on quartz substrates in a low pressure chemical vapor deposition (LPCVD) system to a thickness of 100 nm. Then, the a-Si samples were divided into two sets and crystallized with an excimer laser at various laser energy densities and at substrate temperatures of 300 and 673 K, respectively. The excimer laser was operated at a wavelength of 308 nm and the pulse width was 40 nsec. The average grain size of the resulting poly-Si samples was determined from cross-sectional transmission-electron-microscopy micrographs and atomic force microscopy (AFM) pictures. Information on the density of grain-boundary defects was obtained from EPR measurements. Defect passivation was achieved by exposing the poly-Si samples to monatomic hydrogen generated in an optically isolated remote hydrogenation system at 350 °C for sequences of 1 h until the spin concentration saturated.

In Fig. 1 the average grain size is plotted as a function of the laser fluence, E_{laser}. Completely crystallized films were obtained at laser energy densities larger than 400 mJ/cm^2. Samples prepared at room temperature and with low laser fluence were composed of small grains with an average diameter of 800 Å (triangles in Fig. 1). With increasing laser energy density the average grain size increases and eventually reaches a maximum of ≈ 1.5 μm at 540 mJ/cm^2. At $E_{\text{laser}} > 540$ mJ/cm^2 the grain size decreases to a constant value of 0.25 μm. Substrate heating during the crystallization process influences the dependency of the grain size on laser fluence. The maximum grain-size observed in specimens crystallized at a substrate temperature of 673 K decreases to 1.0 μm and the laser fluence at which large-grained material is obtained decreases by 35 mJ/cm^2 compared to poly-Si samples crystallized at room temperature (diamonds in Fig. 1). In addition, the laser-fluence range in which large-grained poly-Si films are crystallized decreases by approximately 10 mJ/cm^2 and at high laser energy densities ($E_{\text{laser}} > 525$ mJ/cm^2) the average grain size is somewhat larger compared to samples prepared at 300 K (diamonds in Fig. 1). A similar shift of the laser fluence range at which the lateral growth is enhanced was reported previously. In addition, Kim, Im, and Thompson observed an increase of the maximum grain size with increasing substrate temperature.[4] However, this could be due to the fact that they crystallized samples with an oxide capping layer in a single-shot experiment.

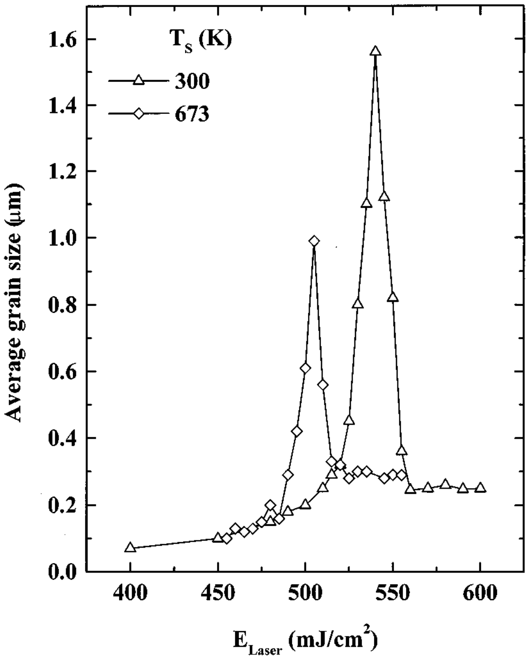

FIG. 1. Average grain size of laser crystallized polycrystalline silicon films as a function of the laser fluence, E_{laser}. The triangles represent poly-Si samples crystallized at room temperature and the diamonds were obtained on poly-Si samples crystallized at a substrate temperature of 673 K.

The concentration of grain-boundary defects measured by EPR is shown in Fig. 2 as a function of the laser fluence. The largest spin concentration of $N_S = 6.7\times 10^{18}$ cm^{-3} was measured on poly-Si samples crystallized with laser energy densities between 400 and 475 mJ/cm^2 at room temperature (open triangles in Fig. 2). The spin concentration is about 3.4 times larger than in solid-state crystallized poly-Si films of the same thickness. With increasing laser fluence the spin density reaches a minimum value of $N_S = 4\times 10^{18}$ cm^{-3} at a laser energy density of 545 mJ/cm^2. It is important to note that poly-Si films crystallized at this laser fluence revealed the largest grain size (see Fig. 1). With further increasing laser fluence a weak increase of N_S is observed due to an increase of the grain-boundary volume.

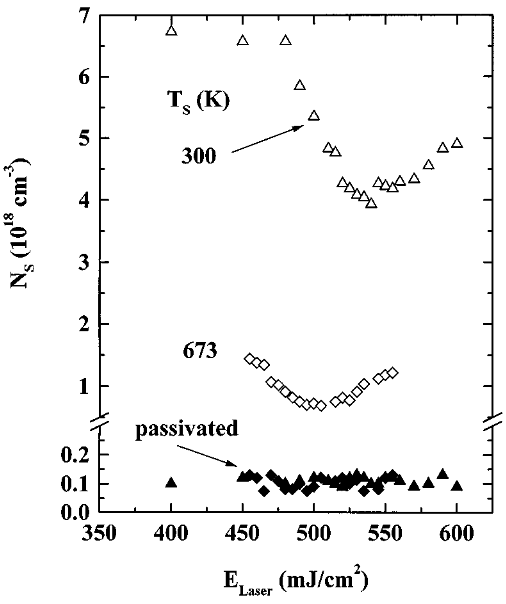

FIG. 2. Spin concentration vs laser fluence, E_{laser}, before (open symbols) and after hydrogen passivation (solid symbols). The triangles and diamonds represent data from samples crystallized at 300 and 673 K, respectively. Hydrogenation was achieved by exposing specimens to monatomic H at 350 K for 2 h.

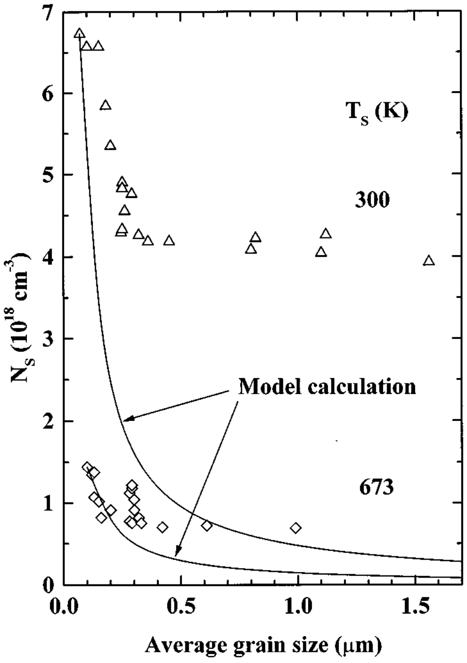

FIG. 3. Spin density vs average grain size. The triangles and circles represent poly-Si specimens laser crystallized at a substrate temperature of 300 and 673 K, respectively. The curves were obtained from model calculations. Details are described in the text.

A pronounced decrease of the spin concentration was observed for all specimens crystallized at a substrate temperature of 673 K (open diamonds in Fig. 2). The largest decrease of N_S by about a factor of 6 occurred at a laser fluence of 540 mJ/cm^2. The dependency of the spin density on laser fluence is similar to that observed for poly-Si crystallized at room temperature. The minimum of N_S is less pronounced but also occurs at the laser fluence that produced the specimen with the largest grains (see diamonds in Fig. 1).

Figure 3 shows the variation of the spin density as a function of the grain size prior to hydrogen passivation for poly-Si samples crystallized at 300 (triangles) and 673 K (diamonds), respectively. For both data sets, the spin concentration decreases with increasing average grain size. However, a significant decrease of the spin density is observed only for samples with an average grain size of less than 0.4 μm. For grains larger than 0.4 μm N_S approaches a constant value asymptotically.

The silicon dangling bonds can be effectively passivated by exposing the poly-Si films to monatomic hydrogen at elevated temperatures. After a hydrogen plasma treatment at 350 °C for two consecutive hours the spin concentration of *all* samples reached a minimum residual value of $N_S \approx 9\times 10^{16}$ cm^{-3} (solid symbols in Fig. 2). It is important to note that the spin density of hydrogen passivated poly-Si is independent of grain size, laser fluence, and substrate temperature during laser crystallization.

A striking feature of the laser crystallization process is the formation of large grains in a small range of the laser fluence for both substrate temperatures. In this process window the average grain size exceeds the film thickness by a factor of 10 and 15 at $T_S = 673$ and 300 K, respectively. The formation of small grains at low laser energies is attributed to heterogeneous nucleation via unmelted silicon.[5] Crystallization of large grains in the small laser-fluence window of 525–550 mJ/cm^2 and 495–510 mJ/cm^2 at substrate temperatures of 300 and 673 K, respectively, is believed to be due to liquid phase regrowth from discontinuous solid islands that are never melted during the crystallization process.[4] At laser energy densities above this regime the silicon film is completely melted and the melt duration increases abruptly. This is strong evidence for supercooling that occurs with rates of more than 10^{10} K/s. The formation of small grains is correlated with this phenomenon.[4,11]

An increase of the substrate temperature causes the following changes of the grain-size dependency on laser fluence: (i) The laser fluence required to achieve very large grains decreases; (ii) the maximum grain size decreases; and (iii) the range of the laser fluence in which large grains can be achieved decreases. The additional energy provided by substrate heating is sufficient to lower the threshold for liquid phase regrowth from discontinuous solid islands and the threshold for complete melting of the silicon film. The excess energy amounts to approximately 3×10^{-17} mJ/cm^2, which is negligible compared to the observed shift in laser energy density by 35 mJ/cm^2. Hence, the excess energy must enhance a yet unknown microscopic mechanism that is essential to laser crystallization. Most likely, this new mechanism is related to hydrogen present in the starting material. Amorphous silicon films prepared by LPCVD still contain up to $\approx 10^{19}$ cm^{-3} H atoms. Most of the hydrogen is accommodated in silicon with binding energies of 1.4–1.7 eV. Most likely, these low-energy configurations are H_{2n}^* clusters.[12,13] In a recent study it was demonstrated, by performing annealing experiments in vacuum and in the presence of monatomic H generated in a plasma, that hydrogen increases the energy barrier for the crystallization of amorphous silicon.[14] Thus, the following picture evolves. At room temperature the ratio of H residing in transport states to H accommodated in clusters is small. A considerable fraction of the energy deposited by an excimer laser pulse is consumed by the dissociation of H clusters and ultimately the evolution of H. This is consistent with results reported on laser dehydrogenation of amorphous silicon.[15] H_{2n}^* clusters are stable complexes and considerable dissociation is observed at temperatures above 350 °C.[16] Hence, substrate heating during laser crystallization enhances the dissociation of large H complexes, consequently lowering the energy barrier for crystallization.

The excess energy provided by substrate heating has a second beneficial effect. All specimens crystallized at a substrate temperature of 673 K reveal a significant decrease of the spin concentration (open diamonds in Fig. 2). Substrate heating enhances the dissociation of H clusters and ultimately the evolution of H, resulting in a decrease of the energy barrier for the crystallization process. The decrease of the H concentration is sufficient to allow for additional reconstruction of Si-Si bonds minimizing the entropy at grain boundaries. However, at the same time the maximum grain-size decreases by about 50%, indicating that the concentration of nucleation sites increases.

Commonly, a change in grain size is accompanied by a change of the grain-boundary defect concentration (see data in Fig. 3). Assuming that grain boundaries comprise approximately two lattice planes and that the defect concentration per unit grain-boundary volume is more or less constant, one can calculate the defect concentration as a function of the grain size. Results of these model calculations are overplotted to the date in Fig. 3 (solid lines). As starting points for our calculations experimentally determined values were used: at 300 K a grain size of 0.07 μm and $N_S = 6.7 \times 10^{18}$ cm^{-3} and at 673 K a grain size of 0.1 μm and $N_S = 1.4 \times 10^{18}$ cm^{-3}. For fine-grained poly-Si the results of the model calculations agree well with the functional dependency of N_S on the grain size. However, for grain sizes larger than 0.4 μm the calculations deviate strongly from the experimental data. The calculations predict a more pronounced decrease of the spin density with increasing grain size. This, however, is not the case. There are two possible reasons that could account for the strong deviations. It is possible that the spin density per unit grain-boundary volume varies from sample to sample. In this case, however, one would not expect a clear dependency of N_S on the grain size. On the other hand, it is more likely that the generation of grain-boundary defects is due to fast solidification and the presence of residual hydrogen preventing the reconstruction of Si-Si bonds. For poly-Si films prepared at room temperature the measured spin density exceeds the calculated values by about a factor of 9.7 for grain sizes larger than 0.6 μm. The difference between data and calculation decreases to a factor of 5.4 for samples prepared at 673 K indicating that substrate heating supports the reconstruction of Si-Si bonds minimizing the entropy at grain boundaries. This observation is consistent with the idea that H effectively increases the energy barrier for crystallization process.

Hydrogenation of poly-Si effectively passivates grain-boundary defects.[17,18] Theory predicts that isolated silicon dangling bonds should be the deepest traps for H. According to local-density pseudopotential calculations, H bonding to an isolated dangling bond results in a low-energy configuration about -2.5 eV below the interstitial bond-centered H.[19] Thus, the observation that the spin density decreases to $N_S \approx 9 \times 10^{16}$ cm^{-3} independent of the preparation parameters is consistent with theory (solid points in Fig. 2). Moreover, the data confirms the idea that during the hydrogenation process an equilibrium is established between defect passivation and defect generation.[18] Defect generation occurs when a single H atom breaks a weak or strained Si-Si bond forming a Si-H bond and a silicon dangling bond.

In summary, we have presented a detailed investigation of the influence of laser-crystallization parameters on grain size and silicon dangling-bond density. Independent of the substrate temperature poly-Si films with an average grain size exceeding the film thickness by more than a factor of 15 were observed. The laser fluence necessary to maximize the grain size decreased by about 35 mJ/cm^2 as the substrate temperature was increased from 300 to 673 K. This is accompanied by a decrease of the maximum grain size by about 50%. Moreover, poly-Si samples crystallized at room temperature reveal a considerably higher spin density compared to specimens crystallized at 673 K. We propose that both effects are due to enhanced dissociation of large H clusters at elevated substrate temperatures. Model calculations of N_S as a function of grain size deviate from the data for grains larger than 0.4 μm. With increasing substrate temperature the deviation decreases indicating enhanced reconstruction of Si-Si bonds at grain boundaries. Since H can effectively prevent the crystallization process,[14] this is most likely due to the dissociation of large H clusters and ultimately the evolution of H. Subsequent hydrogenation of the specimens causes the spin density to decrease to a minimum residual value of $N_S \approx 9 \times 10^{16}$ cm^{-3} independent of substrate temperature and laser fluence. This is consistent with theoretical investigation of H bonding to isolated dangling bonds.

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