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Improvement of grain size and deposition rate of microcrystalline silicon by use of very high frequency glow discharge

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The influence of the plasma excitation frequency on the growth conditions and the material properties of microcrystalline silicon prepared by plasma enhanced chemical vapor deposition at low deposition temperature is investigated. It is found that an increase of the plasma excitation frequency leads to a simultaneous increase of the growth rate, the grain size, and the Hall mobility of microcrystalline silicon. This is attributed to an effective selective etching of disordered material creating more space to develop crystalline grains, while also more species for faster growth of the crystallites are available. © *1994 American Institute of Physics.*

Microcrystalline silicon (μc:Si:H) prepared by plasma enhanced chemical vapor deposition (PECVD) is a promising material for applications in large area electronic devices like thin film solar cells and flat panel displays.[1,2] In addition the material has a potential as a nucleation seed for thin crystalline silicon. The material consists of variable volume fractions of amorphous phase, grain boundaries, and crystalline grains with dimensions from a few tens to a few thousands of angstroms. Microcrystalline silicon is prepared from gas mixtures of SiH_4 and H_2 by PECVD. Thus the deposition process is compatible with the well-established amorphous silicon (a-Si:H) technology. For technical applications a further improvement of, e.g., the carrier mobility, the grain size, and the deposition rate is required. In particular, a correlation between crystallinity and suppressed growth rate is found and an improvement of the grain size is mainly achieved by an increase in the deposition temperature.[3] High temperatures, however, one wants to avoid in amorphous silicon technology and large area electronics.

Recently the use of very high frequency glow discharge was proposed to provide favorable conditions for the growth of μc-Si:H, leading to high quality material at lower plasma excitation power and deposition temperatures.[4–6] So far a comparison of material prepared under similar conditions, where only the plasma excitation frequency is varied, is missing. Here we present an investigation of the growth conditions of phosphorus-doped μc-Si:H for various plasma excitation frequencies (13–120 MHz) and the influence on the material properties.

Samples were prepared in a diode-type reactor with radiation heater, an electrode area of 10×10 cm^2 and an electrode spacing of 1.2 cm. Deposition conditions are 3 sccm SiH_4 (with 2% PH_3), 97 sccm H_2, 5 W externally applied rf power, and substrate temperature of 200 °C. For plasma excitation, a signal generator (0.1–150 MHz), a broad band amplifier (10–125 MHz), and a T-network matchbox with a stepwise variable inductance are used. Optimum matching is achieved by minimizing the reflected rf power at a given frequency and then further adjusting the frequency to decrease the reflected power. This results in power reflection of less than 0.5 W for 5 W forward power. Plasmas were ignited at low power with a high voltage spark. Three series of samples were prepared at 150, 300, and 500 mTorr. Electrical transport is studied by conductivity (coplanar electrode configuration with Ag contacts) and Hall effect (van der Pauw geometry) measurements. Hall mobilities are measured with a modulated current technique because of the small Hall voltages found in the highly conductive doped μc-Si:H material. The average grain size is determined from x-ray diffraction (XRD) at grazing incidence using the Debye–Scherrer formula for the ⟨111⟩ reflex. Raman scattering and transmission electron microscopy (TEM) are used to investigate the crystalline volume fraction and detailed information on the film structure like columnar structures and individual grain sizes.

Stable plasma conditions are only obtained with $p=300$ mTorr for the entire frequency range. At low pressure (150 mTorr) and low frequency, no plasma could be ignited and at high frequencies and high pressure (500 mTorr) the deposition was inhomogeneous over 10×10 cm^2. For all three pressure regimes the deposition rates as a function of plasma excitation frequency between 13.56 and 120 MHz are shown in Fig. 1. We observe a steady increase of the deposition rate by about a factor of 4 from 13.56 to 120 MHz to a maximum rate of 1.1 Å/s. At a given frequency the deposition rate slightly increases with pressure.

All samples show a high degree of crystallinity. This is confirmed by Raman, TEM, and XRD measurements. The intensity ratio $I_c/(I_c+I_a)$ of the Raman intensities at 480 cm^{-1} (I_a) and 520 cm^{-1} (I_c) as a function of the plasma excitation frequency shows a value of about 60%, which corresponds to a volume fraction of $\geqslant$90%. This has been confirmed by TEM and by studies on thermally fully crystallized material.[7] Only at the lowest excitation frequencies the intensity ratio is smaller. This indicates that the crystalline volume fraction is not affected by an increase in the deposition rate in the case of high plasma excitation frequency. In addition, the average grain size as determined by XRD in-

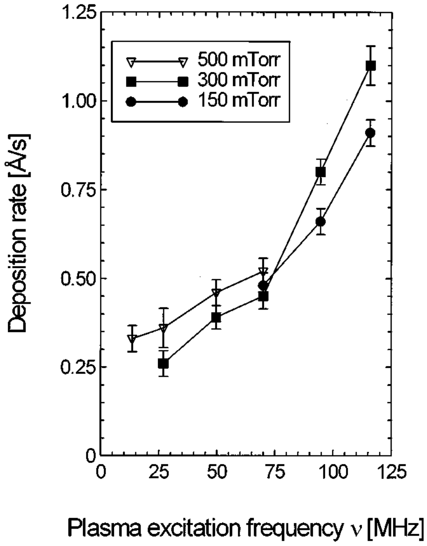

FIG. 1. Deposition rate for μc-Si:H prepared from mixtures of silane in hydrogen with PECVD as a function of the plasma excitation frequency. At a given frequency the deposition rate increases with total gas pressure. The plasma power is kept constant at nominally 5 W.

creases with excitation frequency from 130 Å at 27 MHz to 320 Å at 120 MHz. This is shown in Fig. 2 for the samples prepared at 300 mTorr. Note that XRD measurements only give an average grain size and the straightforward use of the Debye–Scherrer formula can severely underestimate the grain sizes.[3] For identification of individual grains we performed high-resolution TEM studies. A sample prepared at 94 MHz with a thickness of 440 nm shows individual grains of up to 250 Å in width and up to 2000 Å in the growth direction (Fig. 3).

While we find no clear correlation between the average grain size and the absolute value of the electrical dark con-

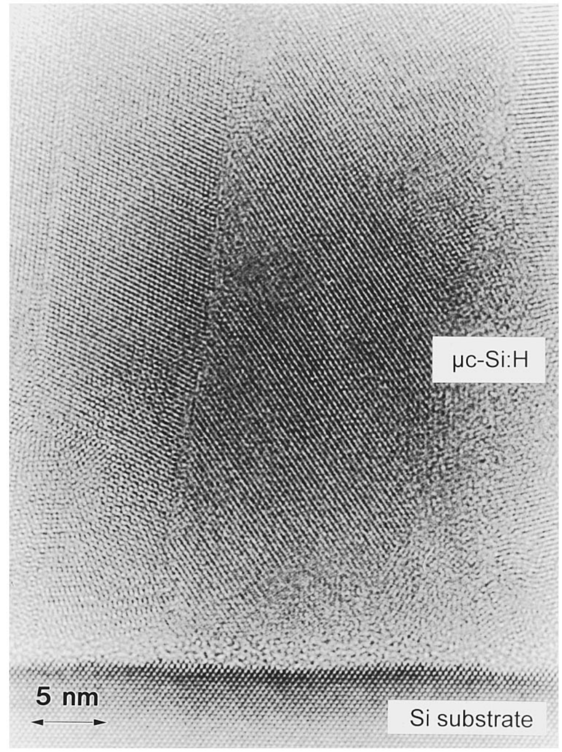

FIG. 3. Cross-sectional high-resolution electron micrograph of a μc-Si:H film deposited at 94 MHz onto a crystalline silicon substrate covered with a native amorphous oxide layer. The detail of the μc-Si:H adjacent to the Si substrate shows grains up to 20 nm width. The crystallites reach a total length of 200 nm (only the lower part is imaged).

ductivity, which is between 30 and 90 S/cm at room temperature for all samples investigated here, the carrier mobility measured by Hall effect shows a steady increase by a factor of 2 with an increase of the grain size. In Fig. 4 the Hall

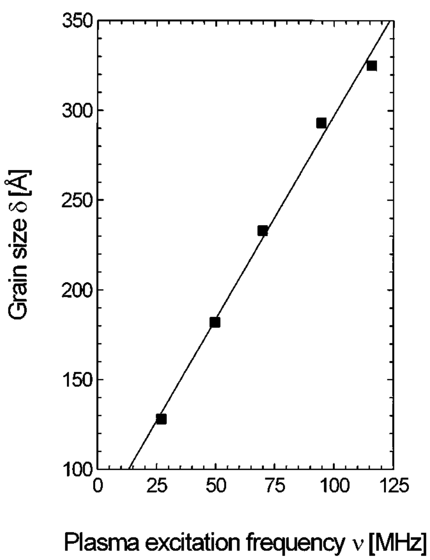

FIG. 2. Average grain size of μc-Si:H prepared with PECVD at various plasma excitation frequencies and total gas pressure of 300 mTorr (compare Fig. 1). The grain size is determined from x-ray diffraction studies applying the Debye–Scherrer formula to the half-width of the ⟨111⟩ reflex.

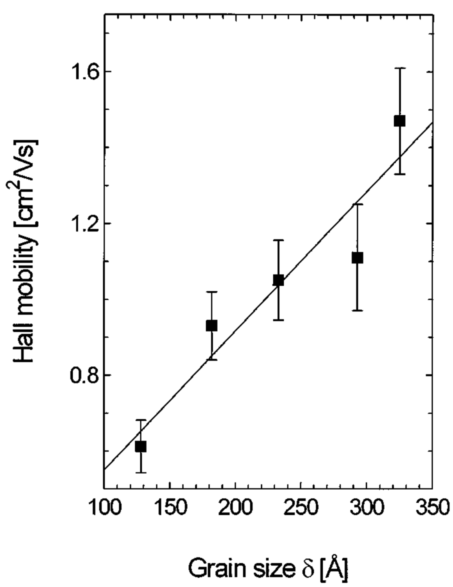

FIG. 4. Hall mobility determined with a modulated current technique as a function of the average grain size for material prepared at various plasma excitation frequencies and a total gas pressure of 300 mTorr (compare Fig. 1).

mobility is shown as a function of the average grain size for the sample series prepared as 300 mTorr. The Hall mobility increases from 0.6 cm^2/V s for material prepared at 27 MHz with an average grain size of 130 Å to a value of 1.5 cm^2/V s for material prepared at 116 MHz with an average grain size of 320 Å.

Thus both grain size and deposition rate of μc-Si:H can be increased by an increase of the plasma excitation frequency in a controllable manner without having to increase the temperature and with a crystalline volume fraction that remains above 90%. The increase in grain size is accompanied by an improvement of the electrical mobility. For an explanation of these results we recall that models for the growth of μc-Si:H with glow discharge techniques generally work with the concept of partial chemical equilibrium[8] or, as a variation of this concept, preferential etching of the amorphous phase.[9,10] Grain sizes are limited by the fact that crystallites grow from many nucleation centers only until they touch an adjacent grain or amorphous material. At low deposition temperatures (200 °C) grains do not coalesce and do not reconstruct at the grain boundaries to form larger grains. Generally a connection between crystallinity and suppressed growth rate is found, i.e., high growth rates prevent crystalline growth.[11] The simultaneous increase of deposition rate and grain size requires that from the very beginning of the deposition, regions between grains (amorphous or grain boundaries), and even some of the crystalline nucleation seeds are effectively etched away to allow subsequent crystalline growth and development of large grains. Further, a sufficient supply of favorable gas phase species is required to obtain a fast growth of crystalline material. The changes in the plasma properties at VHF provide these conditions. There is evidence that high frequency plasmas enhance dissociation in the bulk plasma (with respect to the plasma sheaths), reduce the sheath thickness, and reduce the sheath voltages, i.e., ion energies.[12–15] This means that an increased radical density (hydrogen and advantageous SiH_x precursors) can traverse the sheath with smaller loss to reach the surface of the growing film. These radicals provide both an effective selective etching of disordered material and fast growth of crystalline grains.

We conclude that with the very high frequency glow discharge we have a unique technique that allows to increase simultaneously the growth rate and the grain size of μc-Si:H at low deposition temperature. This is achieved by an effective selective etching of disordered material creating more space to develop crystalline grains, while also more species, for faster growth of the crystallites, are available. A control of growth rate and grain size offers new possibilities for the use of this material in thin film devices and as precursor for nucleation of thin film crystalline silicon.

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