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ANNEALING AND HYDROGENATION BEHAVIOUR OF EVAPORATED AND SPUTTERED HIGH-PURITY AMORPHOUS SILICON FILMS

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Abstract.- Amorphous silicon films have been prepared by ultra-clean evaporation and sputter technique enclosing different amounts of hydrogen into the films. The dark conductivity of both types of films can be reduced from $10^{-2}$ $(\Omega \cdot cm)^{-1}$ as deposited to values smaller than $4 \times 10^{-11}$ $(\Omega \cdot cm)^{-1}$ if the films contain enough hydrogen and are annealed to about 600 K. Close to the annealing minimum of the dark conductivity a maximum of photoconductivity is observed.

Introduction.- It is well known that the incorporation of hydrogen into amorphous silicon films drastically reduces the concentration of the dangling bond states and makes an efficient doping of the material feasible. While a-Si films prepared by glow discharge (gd) decomposition of silane always contains sufficiently hydrogen, for the other a-Si preparation techniques a hydrogenation of the films has to be provided separately. First Paul et al. /1/ produced films which can be doped by reactive sputtering in a hydrogen-argon mixture. Other authors /2,3/ reported about a subsequent hydrogenation by heat diffusion of atomic hydrogen into the film. Miller et al. /4/ added atomic hydrogen during the evaporation process and were able to reduce the room temperature dark conductivity $\sigma_D$ from $10^{-4}$ to $10^{-9}$ $(\Omega \cdot cm)^{-1}$ after a heat treatment. In a previous paper /5/ we already pointed out that structural relaxation processes in ultra-clean a-Si films may diminish the density of the dangling bond states considerably. We did not succeed, however, hitherto to reduce $\sigma_D$ at room temperature much below $10^{-7}$ $(\Omega \cdot cm)^{-1}$.

In this paper we present measurements on a-Si films evaporated in a molecular hydrogen beam, where the hydrogenation takes place during evaporation and in a following annealing treatment. The hydrogenation and annealing behaviour of these films are compared with those prepared by reactive sputtering.

Experimental procedures.- The a-Si films are prepared in UHV based evaporation and sputter equipments. The evaporation system consists of two separated chambers for the e-gun source and for the substrate, respectively. A residual gas pressure of less than $10^{-9}$ torr could be maintained during evaporation with a rate of approximately 4 $\AA$/s. Substrate heat treatment was possible between 10 K and 800 K as well as in-situ dark conductivity measurements. A molecular hydrogen beam collimated by a multichannel nozzle could be directed to the substrate. Much care has been taken to avoid any contamination of the substrate and of the system by the gas inlet system. For the UHV sputter system a commercial rf sputter gun was converted into an UHV compatible version. An Ar or H$_2$ partial pressure up to $10^{-3}$ torr could be admitted without altering the residual gas background for more than a factor of two. Sputter rates of 1-4 $\AA$/s at a distance of 25 cm are obtained by using an Ar working pressure of about $10^{-3}$ torr.

Photoconductivity, thermoelectric power, and ir absorption measurements could be carried out in separate systems.
Results and discussion.- The room temperature dark conductivity is shown in Fig. 1 for various a-Si films as a function of the annealing temperatures $T_A$.

Fig. 1: Room temperature dark conductivity for typical amorphous silicon films prepared by evaporation or sputter technique as a function of the annealing temperature. $T_S$ is the substrate temperature during preparation of the films, $P_{H_2}$ is the effective partial hydrogen pressure, $p_0$ the residual gas pressure (without $H_2$ and Ar) during evaporation or sputtering.

The uppermost curve of Fig. 1 represents the typical annealing behaviour of "not as clean" films prepared by sputter or evaporation technique without hydrogen. The curve beneath shows the reduction of $\sigma_D$ for annealing temperatures up to 600 K, caused by relaxation processes in the clean film. Two facts could not really be cleared up for this film: First, the conductivity minimum around $T_A = 600$ K might be deeper. The experimental data are too scarce in this temperature range. Second, it is still open, whether the conductivity minimum is only due to relaxation processes between silicon atoms themselves, or the very low hydrogen background in these films is already capable to passivate a considerable part of the defect states. Under the same preparation condition an effective partial hydrogen pressure of $2 \times 10^{-6}$ torr is already sufficient to move the $\sigma_D$-minimum below $10^{-9}$ (n$\cdot$cm)$^{-1}$. $\sigma_D$ values as low as $3 \times 10^{-11}$ (n$\cdot$cm)$^{-1}$ can be achieved by increasing the effective hydrogen pressure to $10^{-6}$ torr. This value almost reaches the $\sigma_D = 10^{-12}$ (n$\cdot$cm)$^{-1}$ minimum obtained by reactive sputtering in an Ar + $H_2$ mixture.

The strong decrease of $\sigma_D$ of in hydrogen evaporated samples is attributed to an activation of the molecular hydrogen, that is dissociated and saturates the dangling bonds of silicon, combined with structural relaxation. Fig. 2 shows the content of 'activated' hydrogen measured by the optical absorption of the Si-H wagging vibration at 640 cm$^{-1}$ following Fang et al. /6/.

Fig. 2: Hydrogen concentration of 'activated' hydrogen in an evaporated a-Si sample as a function of the annealing temperature. The concentration was determined by ir absorption of the wagging vibrational band.

According to Fig. 2 a certain amount of hydrogen is already bound in the freshly evaporated a-Si film. With increasing annealing temperature the concentration of active hydrogen first increases. It reaches a maximum with 0.75% at 500 K, at 600 K the hydrogen concentration drops to about 0.6%. The minimum of $\sigma_D$ is always observed around 600 K. At this temperature, which is also favourable for the preparation of...
gd-a-Si samples, a structural change may take place, as proposed by Mattes /7/ with the help of a cluster model. At higher annealing temperatures $\sigma_D$ at room temperature rises rapidly for hydrogenated and non-hydrogenated samples. This rise may be attributed to the loss of hydrogen and simultaneously to a regeneration of defects. The thermo-electric power becomes larger and negative, what indicates a shift of the Fermi level toward the conduction band. If the regeneration of defects is responsible for the rise of $\sigma_D$ for $T_A > 600$ K at all, the regenerated defect distribution can not be symmetrically to the midgap.

The temperature dependence of the dark conductivity $\sigma_D$ presented in Fig. 3 with $T_A$ as parameters shows that variable range hopping transport is dominating for low $T_A$ values at low and moderate temperatures, while activated transport in extended states takes place for $T_A \sim 600$ K (activation energy $E_A \sim 0.8$ eV for curve 4) and at high temperatures.

Fig. 3: Temperature dependence of the dark conductivity of an a-Si film evaporated in hydrogen for different annealing temperatures $T_A$.

A comparison of the annealing behaviour of the dark and photoconductivity of evaporated and sputtered a-Si films in Fig. 4 shows that minimal values of $\sigma_D$ almost correlate with maximal values of $\sigma_{Ph}$. The two maxima of $\sigma_{Ph}$ occurring in either cases may be due to two different photconduction pathes. The photoconductivity reported here is not as high as obtained in gd-prepared /8/ and sputtered /9/ samples by other authors. An optimization of the photoconductivity is still to be carried out.

Finally, Fig. 5 illustrates the decrease of the room temperature conductivity $\sigma_D$ with increasing hydrogen partial pressure.

Fig. 4: The annealing behaviour of the photoconductivity $\sigma_{Ph}$ (illumination with $\lambda = 633$ nm, 2 mW/cm², $6 \times 10^{15}$ photons·cm⁻²·s⁻¹) of evaporated and rf-sputtered a-Si films with high hydrogen partial pressure compared to the variation of the dark conductivity $\sigma_D$ measured at room temperature.

Fig. 5: Temperature dependence of the dark conductivity $\sigma_D$ of gd-a-Si samples at room temperature. The temperature dependence of the dark conductivity $\sigma_D$ is shown after annealing to different temperatures.
Fig. 5: Room temperature dark conductivity versus partial hydrogen pressure for a-Si samples prepared by rf-sputtering ($p_0$ is the residual gas pressure except $p_{Ar}$ and $p_{H_2}$).

Conclusion.- An effective hydrogenation of a-Si-films is possible by ultra-clean evaporation technique in a $H_2$ beam and subsequent annealing to 600 K similar as by reactive sputter technique. Dark conductivity values as low as $3 \times 10^{-11} \, (\Omega \text{cm})^{-1}$ for evaporation and $10^{-12} \, (\Omega \text{cm})^{-1}$ for sputtering are correlated with a maximum of photoconductivity.

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