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Effect of a hydrogen plasma on various a-Si : H_x structures at low temperatures

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Résumé. — Nous montrons la possibilité de modifier les propriétés électroniques de films a-Si : H maintenus à 190 °C en les soumettant à un plasma d'argon-hydrogène. Nous indiquons la variation du contenu en hydrogène, du gap optique et de l'énergie d'activation suivant la durée de l'interaction film-plasma.

Abstract. — The possibility of changing the electronic properties of a-Si : H films by contact with a hydrogen argon plasma at 190 °C is demonstrated. The variation in hydrogen content, optical gap and conductivity *versus* 1/T for increasing interaction, times is reported.

The hydrogen concentrations at various hydrogen sites in amorphous hydrogenated silicon (a-Si:H) may be considered as guide marks to the structure of the silicon matrix which controls the electronic properties of this material [1]. They can be modified by hydrogen entrance into, or exodiffusion from the basic silicon matrix.

The optimization of the interesting properties of a-Si : H (doping and space charge zone capability) requires relatively critical silicon matrix structures, with very few localized states, and hence it might be interesting to adjust *a posteriori* the hydrogen content at the various hydrogen sites in an attempt to attain optimum structures.

A decrease in hydrogen concentration can be achieved by annealing in vacuum, and an increase in hydrogen concentration by annealing in a hydrogen plasma.

Previous work has demonstrated the possibility of introducing hydrogen atoms from a plasma into a solid Si matrix at high temperatures, ~ 500 °C, in materials fully depleted of hydrogen, either a-Si : H film dehydrogenated by high temperature annealing under vacuum [2] or pure a-Si films [3]. We will show here the possibility of increasing significantly step by step the total hydrogen content of films having initially more than 13 % of hydrogen and a very low spin density ($< 10^{17} \text{ cm}^{-3}$), using a soft RF plasma and a low sample temperature (190 °C). The same procedure is also efficient for introducing hydrogen at 190 °C into pure a-Si films, as will be reported

elsewhere. As hydrogen will be partially included on bonded sites (mainly SiH), this implies unambiguously a low activation energy for the relaxation of the Si matrix. Such low activation energies for the relaxation of the Si matrix were already described from the exodiffusion of hydrogen [4], and from the possibility of fast hydrogen diffusion at low temperature (190 °C) from a-Si : H to other adjacent solid films (e.g. pure a-Si and Pd) [5].

The films are prepared by RF diode cathodic sputtering onto a crystalline silicon substrate maintained at 190 °C, from a Si target in an argon gas (a-Si) of 20 % H₂/80 % Ar reactive gas a-Si : H) at

$$9 \times 10^{-3} \text{ torr}.$$

We may vary the structure of the Si matrix, and so in the latter case, the hydrogen concentration [1] at the various sites, by varying the deposition rate between 10 Å/min and 130 Å/min. The deposition rate (*R*) depends linearly on the DC polarization induced by the RF voltage between the substrate holder and the target. For DC voltages of 1 500 V, 400 V and 300 V, we have respectively

$$R = 130 \text{ Å/min} \quad H \sim 13 \%;$$

$R = 10 \text{ Å/min} \quad H \sim 30 \%$ and $R = 0$. Lower DC voltages sustain a hydrogen-argon plasma down to ~ 200 V. We will describe here the variations in the total hydrogen content *H*, and its distribution among the various hydrogen sites, the optical gap E_0 , and the electrical conductivity *versus* reciprocal temperature for films deposited at $R = 70 \text{ Å/min}$ (~ 1 000 V) at 190 °C and at this temperature in contact with a

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hydrogen-argon plasma $V = 200$ V during increasing time in the same vacuum chamber.

In virgin films, the distribution of hydrogen between various sites in the Si matrix depends strongly on the deposition rate [1]. These sites are defined from infrared absorption of the stretching mode of the silicon hydrogen bond around $2\,000\text{ cm}^{-1}$ and $2\,100\text{ cm}^{-1}$ respectively for SiH and SiH₂ sites [6] and the balance [1] between the total hydrogen content and the concentrations of hydrogen at SiH or SiH₂ sites (after calibration of the oscillator strengths of the $2\,000$ and $2\,100\text{ cm}^{-1}$ vibration modes and with the hypothesis that they do not depend on R).

For $R \approx 30\text{ Å/min}$, all the hydrogen atoms are bonded as SiH ($\sim 70\%$) or SiH₂ ($\sim 30\%$). For $R \sim 120\text{ Å/min}$, we found a significant amount of hydrogen ($\sim 30\%$) not bonded as SiH and SiH₂. We called this (these) other site(s) H'. Other sites might be for instance hydrogen with two silicons in a three centre bonds configuration [7] or pure interstitial hydrogen.

The unit tetrahedral cell of silicon is characterized by the sp^3 hybridization of the silicon s and p orbitals which needs a silicon atom bonded with four other silicon atoms. Where silicon is bonded to another atom, this bond obviously does not exhibit sp^3 hybridization, but the character of the three other bonds are also modified and in consequence the lengths and angles of these bonds also modified. This effect is well known in crystalline silicon [8], where the occurrence of the surface introduces reconstructed bonds between the broken orbitals, but also back bonds with the silicon atoms of the second layer, both giving localized states.

Hence each hydrogen whose electron participates in an orbital with those of silicon introduces a deformation in the silicon matrix. The deformation depends on the nature and number of the silicon hydrogen bonds.

The hydrogen concentration at the various hydrogen sites may therefore be considered as guide marks for the structure of the silicon matrix defined as the relative sites of silicon atoms in a-Si:H. In addition, other intrinsic deformations of the silicon-silicon bonds are introduced by the disorder so that the electronic properties of a-Si:H are controlled by the concentration of hydrogen on SiH or SiH₂ or H' sites only over very restricted preparation ranges, where the other deformation sources can be considered as constant [1]. The total hydrogen concentration in the film is measured by the resonant nuclear reaction with Boron [1] $B^{11} + H \rightarrow \alpha + Be^*$.

Figure 1 shows hydrogen concentration versus depth for films deposited at 70 Å/min and after a plasma (200 V.D.C.) during 0 min (—), 10 min (---), 60 min (---). There is a 2 to 3 % higher hydrogen concentration near the surface (200 Å) then a slight increase with depth.

Fig. 1. — Hydrogen concentration versus depth in films after post-hydrogenation during 0 min (—), 10 min (---), 60 min (---).

The hydrogen concentration at a depth of $5\,000\text{ Å}$ increases from 15.7 % for $t = 0$ to 18 % for $t = 10$ min and to 19 % for $t = 60$ min.

After the interaction of a film with hydrogen plasma, there is always a higher H on the a-Si:H surface (erf function with $\sigma = 150\text{ Å}$) which appears especially important for low hydrogen concentrations ($< 10\%$) (i.e. for post hydrogenation of pure a-Si, 13 % in the surface, 1 % in the bulk), then a nearly constant concentration in the bulk of the film.

Three other films deposited at 70 Å/min and annealed at 190°C in the same hydrogen-argon plasma also saturate their total hydrogen content in the 18 %-20 % range.

For these films, there is at each temperature an upper limit for the equilibrium value of their total hydrogen content, irrespective of their sites [4], which is 21 % at 190°C . The H in these films increases when they remain over increasingly longer periods of time in contact with the plasma, but saturates towards this limit value.

Quite generally, after contact with a hydrogen-argon plasma, both the total hydrogen concentration and the relative concentration at the various hydrogen sites depend strongly on the virgin silicon matrix structure, controlled here by the deposition rate and the deposition temperature.

At a deposition rate of 70 Å/min , there is only small changes in the hydrogen concentration at SiH or SiH₂ sites, but an increase in the number of H' sites.

Whatever be the deposition rate and the hydrogen site whose concentration is varied, the structure of the virgin silicon matrix is changed after post-hydrogenation, and this in turn induces changes in the electronic properties of the material. For instance, figure 2 shows the variation of the optical gap (taken here as the photon energy corresponding to an optical absorption coefficient of 10^4 cm^{-1}) versus post-hydrogenation time. The optical gap increases from 1.6 eV to 1.9 eV for « 0 » to « 60 min » of post-hydrogenation, here with the additional number of H' sites. An increase in the optical gap with the number of H' sites, however with a smaller efficiency, was previously found in virgin films corresponding to $21\% < H < 35\%$ and $R < 20 \text{ Å/min}$. In these films, there was at the same time a decrease in the number of hydrogen atoms bonded as SiH or SiH₂. This suggests that although H' sites change the structure of the Si matrix, they are in this way less efficient than bonded SiH or SiH₂ sites.

Fig. 2. — Optical gap E_0 versus post-hydrogenation time.

Figure 3 shows the variation in conductivity with temperature as the post-hydrogenation time increases.

The validity of coplanar measurements of the electrical conductivity and of its activation energy was recently questioned [9]. We report here electrical conductivity measurements in a sandwich cell configuration. We show elsewhere [5] that good ohmic contacts can be achieved by progressively introducing a large amount of localized states in the a-Si:H gap in the vicinity of its interfaces with other materials, by progressively depleting a sufficient amount of hydrogen. This can be obtained, for instance, by diffusion of hydrogen at 190°C from a depth of 400 Å in the a-Si:H towards adjacent films of pure a-Si or Pd.

Actually for $\sigma(1/T)$ measurements, these a-Si:H films of 9000 Å were deposited on a-Si films of 1000 Å and covered by another Pd film evaporated in a high vacuum unit.

For $t = 0$, the conductivity at 300 K is

$$1.2 \times 10^{-11} \Omega\text{cm}^{-1}$$

with an activation energy of 0.71 eV , for $t = 10 \text{ min}$, the σ_{300} decreases to $5 \times 10^{-12} \Omega\text{cm}^{-1}$, while its activation energy increases to 0.76 eV , to finally reach $\sigma_{300} = 8 \times 10^{-13} \Omega\text{cm}^{-1}$ with $E_a = 0.79 \text{ eV}$ for $t = 60 \text{ min}$.

Fig. 3. — Conductivity σ versus reciprocal temperature after post-hydrogenation during $t = 0 \text{ min}$ $E_a = 0.71 \text{ eV}$, $t = 10 \text{ min}$ $E_a = 0.76 \text{ eV}$ and $t = 60 \text{ min}$ $E_a = 0.79 \text{ eV}$.

In virgin glow discharge a-Si:H films and over a restricted preparation range, Solomon *et al.* [10] found the same variation for E_0 and E_a . They conclude that the Fermi level in this material was pinned by some intrinsic defect, always at the same distance from the valence band.

Here, the increase in the activation energy E_a of the conductivity is smaller than the increase in the optical gap E_0 . The introduction of hydrogen has modified the Si matrix and therefore the distribution of the localized states which controls the Fermi level.

In conclusion, the experimental results reported here are consistent with a general picture according to which the silicon matrix controls the electronic properties of the material, optical gap and distribution of localized states. Therefore hydrogen entrance into the material, even away from the bonded SiH or SiH₂ sites, modifies the silicon matrix, and hence the electronic properties of the material.

However, the Si matrix structure in the virgin films depends on preparation conditions, in particular, the deposition rate (R) and temperature (T_s). We show here, for given R and T_s , the possibility of

using post-treatment to continuously vary the optical gap and the activation energy for electrical conductivity of such a material. We are now looking for the variation induced in the distribution of localized states, which will ultimately limit the performance of a-Si:H based devices.

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