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Thickness dependence of hydrogen in a-Si : H films deposited on c-Si

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Résumé. — Nous avons mesuré la concentration totale d'hydrogène et la concentration d'hydrogène lié en SiH et SiH₂ en fonction de l'épaisseur, d , de films de a-Si : H déposé sur c-Si avec des épaisseurs variant de 0,2 à 1,6 μ . Le contenu relatif d'hydrogène lié varie de ≈ 1 ($d \leq 0,2 \mu$) à un minimum de 0,5 ($d \approx 0,6 \mu$) pour atteindre ensuite une valeur presque constante ($\sim 0,8$) au-dessus de 0,9 μ . Il y a une décroissance significative $\sim 5\%$ du contenu total en hydrogène quand l'épaisseur croît jusqu'à 0,5 μ . Ces effets sont discutés en relation avec notre modèle sur le rôle de l'hydrogène dans ce matériau.

Abstract. — We have measured the total hydrogen content and the concentration of hydrogen bonded as SiH or SiH₂ versus the thickness, d , of a-Si : H films deposited on c-Si from 0.2 μ to 1.6 μ . The relative ratio of bonded hydrogen decrease from ≈ 1 ($d \leq 0.2 \mu$) to a minimum of 0.5 ($d \approx 0.6 \mu$) then reaches a nearly constant value of 0.8 above $d \approx 0.9 \mu$. There is a significant decrease of the total hydrogen content ($\sim 5\%$) in the lower thickness range ($d < 5\,000 \text{ \AA}$). These effects are discussed in relationship with our previously published model on the role of hydrogen in this material.

1. Introduction. — One recurring problem in the amorphous hydrogenated silicon literature is that the electrooptical properties of reactive-sputtered and glow discharge materials seem to vary considerably between laboratories even though fabrication conditions are carefully controlled to try to reproduce published materials. Sample reproducibility difficulties originating from different deposition and shielding geometries giving different plasma properties and different possible degrees of contamination are often cited as being responsible for these differences [1]. Band bending in the vicinity of substrate or surface was also invoked [2]. We have shown that the electronic properties of sputtered a-Si : H depend mainly on the « structure » of the silicon matrix, which can be changed through the substrate temperature, the deposition rate [3] and by posthydrogenation [4, 5] and that the hydrogen concentration and site give an image of this structure [6]. Most of the samples

have been very thin films, generally $\leq 1 \mu\text{m}$ in thickness. Often, samples which are being compared have not been of identical thicknesses. We have been interested in determining what effect sample thickness may have on the compositional and H bonding properties of these films. Are there significant surface or substrate effects and compositional heterogeneity in 0-1 μm samples? Preliminary results [7] suggest inhomogeneous distribution of the silicon matrix deformations near the film interfaces with neighbouring films.

To study more systematically this point, we prepared series of samples of differing thicknesses with all other fabrication conditions fixed. All samples were deposited on c-Si, studied by hydrogen compositional profiles using elastic recoil detection of protons ejected by a beam of 30 MeV ³⁵Cl ions, and nuclear reaction with boron, and by the mean silicon-hydrogen bonds concentrations detected by infrared absorption.

The results of our study reveal important sample heterogeneities which might have very important ramifications for devices using this material and for the validity of the simple homogeneous models used to interpret electrooptical measurements. Our results are quite reproducible from run to run but apply only to *one* set of material fabrication conditions of interest for device preparation. We are at present pursuing this study to determine the range of material fabrications conditions in which these heterogeneities persist.

2. Experimental design. — Amorphous hydrogenated silicon samples used in this study were prepared using a special RF sputtering apparatus to decrease contamination and to allow detailed comparison of films of variable thicknesses. We use liquid nitrogen zeolite traps, then liquid helium pump to minimize the contaminant level. In the uniform deposition zone of the reactor we placed a sample holder containing 4 pairs of substrates and a three-positions masking system which would expose the first two pairs only for the deposition, then the second and third pair only and finally the third and fourth pair only. Films of various thicknesses were obtained by varying the deposition time. This procedure was taken to ensure that the plasma deposition parameters remained constant throughout the deposition since the vacuum was broken only after the four pairs were made. From size limitation within the vacuum chamber, it was difficult to have series of more than four samples pairs of different thicknesses in the same run. We believe that we succeeded once and we show below the results for different sample pairs of varying thicknesses between 0.05 and 1.9 μm . For analysis, we chose as substrate pairs 1 000 $\Omega\text{ cm}$ polished crystalline silicon wafers and polished fused silica discs.

The base pressure was 10^{-6} torr and the reactive gas of 80 % argon and 20 % hydrogen was maintained at 8 mtorr by an automatic microleak with a constant flow rate. The substrate temperature was always 190 °C. For the films under study the deposition rate, v , presents almost a linear relationship with the target voltage [3]. We used a rate of 70 $\text{\AA}/\text{min}$. $\pm$ 5 $\text{\AA}/\text{min}$.

All samples deposited on c-Si were analysed by nuclear elastic recoil detection [8] to determine hydrogen compositional profiles. Secondly, we studied the optical transmission spectra from the visible through to the infrared range using first the fused silica substrates then the silicon substrates.

From the interferences fringes in the visible and IR region, the index of refraction and then the sample thickness were determined. They are in good agreement with the values derived independently from the nuclear experiments.

The concentration profile of atomic hydrogen [H] was measured by analysing the energy spectra of

hydrogen recoiling from elastic collisions with incident ^{35}Cl atoms of about 30 MeV [9]. This technique is very accurate and requires only about 20 min. for analysis of H concentration in the 10 % range. Some profiles were checked at a selection of depths with the more time consuming resonant nuclear reaction of boron with hydrogen

which in turn is calibrated from the known concentration of hydrogen atoms in mica sheets.

The hydrogen concentrations of SiH or of SiH₂ sites of these films were derived from the infrared absorption of the corresponding stretching modes around 2 000 and 2 095 cm^{-1} . These stretching modes were studied through the transmission curves in the range 2-9 μ using a Beckman IR4240 double beam spectrophotometer and a deconvolution procedure described in some detail in a previous article [3]. In a typical transmission recording, the 2 000 cm^{-1} mode, usually attributed to the SiH site [10, 11] dominates. By subtracting the pure SiH absorption component from the total absorption curve, we obtain the absorption which is ascribed to the SiH₂ component (the temperature $\sim$ 200 °C prevents the occurrence of SiH₃ [11], the independent variation of the concentrations of dangling bonds and the SiH₂ stretching mode prevents the presence of (SiH₂)_n [11]). This deconvolution procedure was used systematically to estimate the concentration of hydrogen bonded either as SiH or SiH₂ with the hypothesis of constant oscillator strengths when the film thicknesses vary.

3. Experimental results. — The hydrogen composition profiles of one of the three series of samples deposited at rates of 70 $\text{\AA}/\text{min}$. are shown in figure 1. The vertical axis gives the total hydrogen content defined by $100 \times [\text{H}]/[\text{Si}]$ and the horizontal axis gives the depth within the sample assuming a mean value for the stopping power of silicon (which depends on the local Si density).

The depth resolution is given by the width of the rise of the hydrogen percentage profile at the free surface and corresponds to roughly 0.02 μm . The profile of the thinnest sample (i) shows a rapid rise to a maximum and an equally sharp drop at the substrate surface. The thickest sample (iii) shows a rise at the free surface which is as sharp as in the thin sample, but to a lower value than that of sample (i). This is followed by a region representing 3/4 of the sample thickness in which the percentage slowly rises linearly towards the substrate interface. Then there is an increase of hydrogen content near the substrate, but the maximum value is still lower than that of sample (i). Finally, in the last 0.1 μm or so, the percentage falls to zero, not abruptly but with a finite slope. This appears to be a real feature and not due to straggling of the incident beam which is less

Fig. 1. — Total hydrogen content *versus* depth in four a-Si : H films deposited in the same run (i, ii, iii, iv) onto c-Si from 30 MeV ^{35}Cl forward diffusion.

than the instrumental resolution for the scattering geometry we used.

The two other samples (ii) and (iv) present profiles intermediate to those of (i) and (iii) described above. The variation of the profiles with thickness is very pronounced up to 0.5 μm then the changes become relatively minor.

The mean total hydrogen content *versus* film thickness is plotted on figure 2 for the 4 samples of figure 1 (∇) and for those of 2 other runs in identical conditions. The thickness ranges overlap between the various runs. As the thickness increases, there is first a decrease from $\approx 17\%$ to 13% ($\sim 0.6\mu$) then a nearly constant value close to that found for this deposition rate in our other RF diode reactive cathodic sputtering apparatus [3].

To see if this compositional heterogeneity corresponded to variations in the silicon-hydrogen bonding and consequently in the electrooptical properties of this semiconductor we measured the percentage of SiH and SiH₂ bonds in these films differing only by their thickness. The results appear in figure 2. Plotted

Fig. 2. — ∇ mean total hydrogen content (H) *versus* film thickness from nuclear experiment. Mean hydrogen concentration on SiH site (O, H₁) on SiH₂ site (+, H₂), on SiH or SiH₂ site (dotted line H₁ + H₂) *versus* film thickness from infrared measurement for a-Si : H deposited on c-Si.

as a function of sample thickness in microns, mean percentage of hydrogen bonded in the SiH configuration (O), mean percentage of hydrogen bonded in SiH₂ configuration (+), and finally mean percentage of bonded hydrogen as detected by IR transmission spectra (i.e. sum of the previous two curves, indicated by dash-dotted line). The IR oscillator strengths are assumed here to be independent of film thicknesses. We use the same values as in our previously published work [3, 6]. This assumption is supported by several independent experiments where the same hydrogen concentration was deduced from infrared and nuclear experiments in quite different conditions : (i) Hydrogen saturated virgin sputtered films (low deposition rate) [H] $\sim 20\%$ [3, 6]; (ii) Posthydrogenated sputtered films (high deposition rate) [H] $\sim 8\%$ [5]; (iii) Posthydrogenated LPCVD films [H] $\sim 1\%$ [12]. In the lower thickness ranges ($d < 0.3\mu$) stress in silicon matrix may introduce additional charge transfer which in turn may affect the oscillator strengths. However, the qualitative features of the curves will remain.

In figure 2, the mean total hydrogen percentage as determined by IR absorption is less precise than that measured by nuclear techniques especially in the lower thickness range as shown by error bar on the figure. However, it is clear that near 0.65 μm there is a significant difference as the total IR content of bonded hydrogen is half of the value deduced from ^{35}Cl measurements. As the film thicknesses decrease below 0.5 μm , there is an increasing amount of H bonded to Si merging in complete bonding below $\sim 0.15\mu$. The curves of hydrogen bonded in SiH and in SiH₂ bonds are nearly constant *versus* depth above 0.9 μ and give values close to those obtained with similar deposition rate in our other deposition apparatus [3]. Higher deposition rates give qualitatively similar results.

The concentration of hydrogen on the various sites vary linearly with a-Si : H thickness only above 0.9 μ . This was the thickness range systematically used in our previous works [3] and our present results agree with these ones. In the lower thickness range ($d < 0.65\mu$) there is an increase in the total hydrogen concentration and in the relative ratio of hydrogen bonded as SiH and SiH₂ when d decreases. Within our picture according to which the hydrogen is linked to Si structural defects this means that the density and the nature of these defects change for low thicknesses.

4. Conclusion. — The above experiments all show that important compositional heterogeneities exist in thin films of amorphous hydrogenated silicon deposited on c-Si. These heterogeneities exist both in chemical composition of the material and in the nature of the bonding between silicon and hydrogen. These variations are very pronounced in our sputtered samples when films are below 0.65 μm thick. This

heterogeneity has very important consequences as most research and device development using this deposition technique has been based on this films in the range 0.5 to 1 μ thick. At the moment, we can only speculate on the detailed causes of these variations and especially the effect of the nature of the substrate. Clearly, if one wishes to study bulk amorphous hydrogenated silicon the film thicknesses should be far thicker than 0.65 μ m and also *interface* effects due to

these heterogeneities have to be carefully studied and separated from those bulk properties being sought.

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