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STRUCTURAL PROPERTIES OF LI-DOPED HYDROGENATED AMORPHOUS SILICON

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Interstitially doped a-Si:H films were prepared by in-diffusion of lithium at T_D=230°C and 320°C, respectively, and characterized by infrared and Raman spectroscopy, ellipsometry measurements as well as SIMS analysis and thermal effusion. Two new infrared modes at frequencies of about 1600 cm^{-1} and 1400 cm^{-1} are observed which we attribute to LiOH and LiH in the near surface region. The decrease of the SiH infrared-absorption peaks and the observation of a new mode in the Raman spectra at 620 cm^{-1} which we attribute to a SiLi alloy suggest an exchange reaction between Li and bonded hydrogen. Changes of the dielectric function in the visible spectral region show that this material contains Li precipitations which give rise to an enhanced Raman scattering cross-section. The results also suggest that lower diffusion temperatures lead to more pronounced Li clustering.

1. INTRODUCTION

Hydrogenated amorphous silicon films doped interstitially by in-diffusion of lithium after film deposition shows all signatures of n-type doping and are an interesting alternative to substitutional phosporus-doping. Many electronic properties are quite similar to P-doped a–Si:H: The temperature dependence of dark conductivity and thermoelectric power[1] as well as the increase of the photoconductivity when the Fermi level is shifted towards the conduction band[2]. In both substitutionally and interstitially doped films the same correlation between the dangling-bond defect density and the Fermi-level position E_C-E_F exists which is also found after stepwise out-diffusion of lithium[3]. This has shown that the formation of defects is independent of the type of donor and it supports the idea of defect equilibration in doped a-Si:H.

In contrast to these similarities, Li-diffused a-Si:H with a Fermi-level position in the upper half of the gap shows a new ESR-signal at $g \approx 2.0061$[4]. This signal is presumably correlated with Li-precipitations occuring mainly in the surface and interface region of films which contain high Li-concentrations. Compared to the electronic properties of Li-doped a-Si:H, little is known about the structural properties and the bonding configurations of Li in a-Si:H. These latter questions are addressed in the present paper.

2. SAMPLE PREPARATION

Undoped a-Si:H films of 1μm thickness were deposited on quartz and crystalline-silicon substrates by rf-glow discharge of SiH_4 under optimized conditions[3] at a substrate temperature T_S=250°C and were then pre-annealed at 350°C for 1h. At T_D=230°C (320°C), respectively, nominal Li concentrations of about 5% were evaporated onto the surface of the films and allowed to diffuse into the samples for about 2h (1h). Afterwards the films were rinsed in HF and water to remove remaining Li-Oxyde and metallic Li from the surface. Undoped reference samples were prepared using the same pre-annealing and HF treatment.

SIMS analysis yielded an average Li concentration of $\approx 10^{18}$ cm^{-3} in the bulk of films with T_D=230°C and $\approx 10^{20}$ cm^{-3} in those with T_D=320°C. In the surface and interface region of the films the Li density is about one order of magnitude larger. This is a general observation in Li-diffused a-Si:H films[4,5].

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3. RESULTS AND DISCUSSION

The infrared spectra of Li-diffused films prepared at T_D=230°C and 320°C look very similar and show new interesting features. For example in Fig.1 (lower curve) we have plotted the difference spectrum of a Li-diffused film with T_D=320°C and a reference sample. This spectrum clearly reveals two new absorption modes at frequencies of about 1600 cm^{-1} and 1400 cm^{-1}. The frequency of about 1400 cm^{-1} agrees well with that of free LiH molecules (1406 cm^{-1}) so that it is most likely due to LiH which has formed in microvoids. The observed splitting of the 1400 cm^{-1} band could indicate that LiH molecules exist in slightly different enviroments (e.g. voids of different size). The second absorption peak at about 1600 cm^{-1} is believed to originate from the OH bending mode in LiOH which should be similar to that of H_2O found at 1595 cm^{-1}. Another possibility is that LiOH is present in water-decorated form (LiOH·n(H_2O)) and that the 1600 cm^{-1} band is due to the decorating water molecules whose oscillator strength is enhanced by the polar LiOH molecule. Both new modes seem to be surface related since they disappear after strong HF treatment.

Another interesting feature are the Si-O related bands between 1050 and 1200 cm^{-1} in the spectrum of the undoped reference sample, Fig.1 (upper curve). As seen in the difference spectrum (lower curve) the interstitial oxygen vibrations at frequencies from 1050 to 1100 cm^{-1} seem to be unaffected by Li diffusion. In contrast to this, the SiO_2 mode at about 1200 cm^{-1} is decreased. Since stoichiometric SiO_2 exists mainly at the interface to the Si substrate, this seems to indicate that the high Li concentration at the interface seen in SIMS react with the oxide under formation of Li_xO complexes. Unfortunately, we were not able to clearly resolve a particular LiO-related vibration for example the $(LiO)^+$ complex which is seen in crystalline silicon at ≈1000 cm^{-1} and is known to act as a shallow donor[6]. The occurence of $(LiO)^+$ in a-Si:H obviously would be of importance for an understanding of the Li-doping mechanism since the actual donor site or configuration is not known.

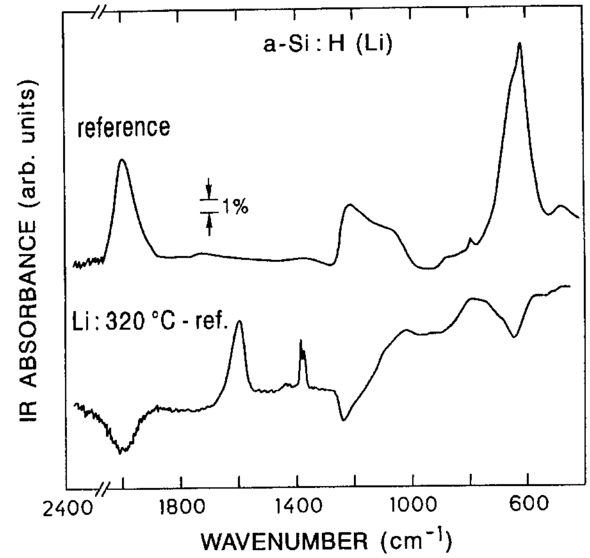

Fig. 1: Infrared absorption of an undoped a-Si:H reference film (above) and the difference spectrum of a Li-doped (T_D=320°C) and a reference film (below).

Furthermore, we observe a decrease of the SiH related vibration modes at 2000 cm^{-1} and 630 cm^{-1} as seen in the difference spectrum, Fig.1 (lower curve). Since the films were pre-annealed at a temperature higher than T_D, this decrease cannot be due to thermal hydrogen effusion (see also the H effusion data in Fig.3a). Instead, a reaction between Li and bonded H must have occured. The simplest reaction is the Li-induced release of hydrogen followed by the formation of LiOH or LiH. Another possible reaction could be an exchange of Li and bonded H under the formation of SiLi. We did not observe a vibrational mode in the infrared spectra which could be definitely assigned to SiLi, but some evidence from Raman spectroscopy will be discussed later.

An additional form of lithium in a-Si:H which has been discussed as a potential reservoir for interstitial Li are small clusters or larger precipitations of metallic Li[4]. By optical spectroscopy we were able to see a strong increase of spherical structures with diameters up to 1 μm in Li-diffused a-Si:H. The existence of metallic clusters in a-Si:H should have consequences e.g. for the optical properties of the samples. In fact, we have observed a change of the dielectric response in the visible spectral

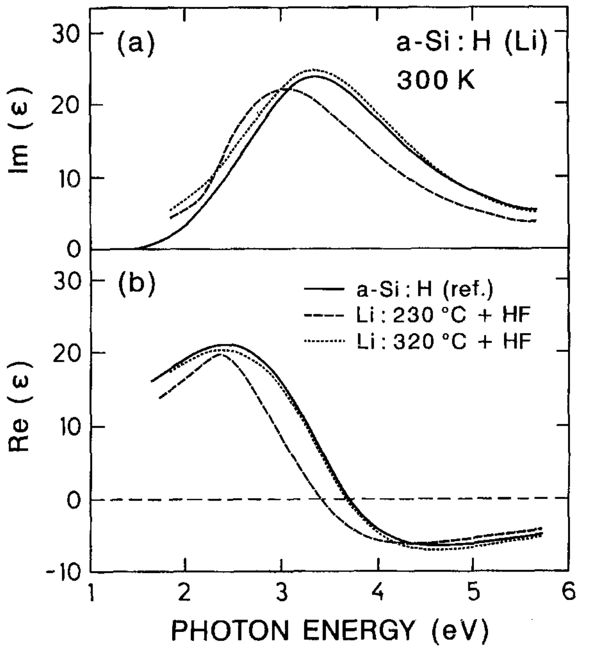

Fig. 2: Real- and imaginary part of the dielectric function ε as measured by ellipsometry for the undoped reference film and two Li-doped films with T_D=230°C, 320°C.

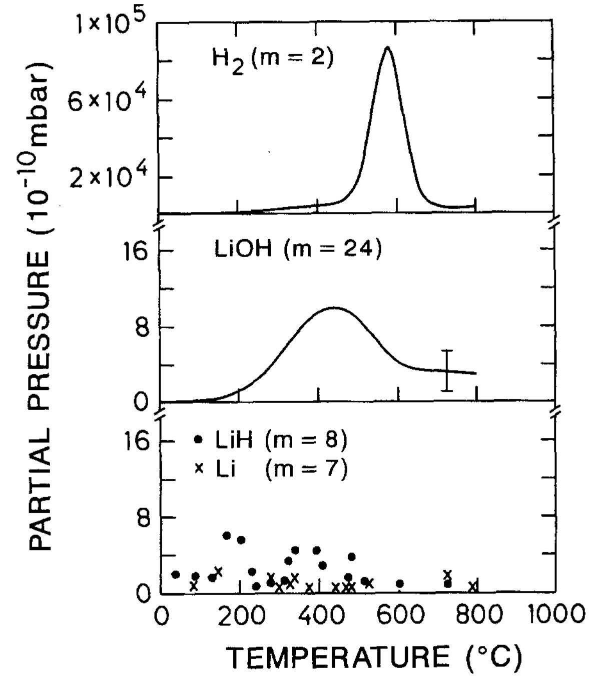

Fig. 3: Thermal effusion of Li-doped a-Si:H films with T_D=360°C.

region between 2 eV and 3 eV for both types of Li-doped films as shown in Fig.2. The change in the dielectric functions can be described by an additional contribution due to a metallic system with a plasma frequency of about 2.5 eV. Such a low value can be expected for small Li spheres embedded in the polarizable Si-matrix ($\epsilon \approx 10$).

Note that the spectra of the sample with T_D=230°C show a larger discrepancy with respect to the reference sample than the one with T_D=320°C. This indicates that for the lower T_D the film is strongly affected although the Li concentration is smaller in this film. This suggests that at higher diffusion temperatures Li precipitates in smaller clusters so that the change of the Si-network structure is smaller. This conclusion is confirmed by the results on Li^+-implanted a-Si:H[4] which show no ESR signal at $g \approx 2.0061$. The reason probably is that Li is distributed in the form of isolated ions or small units of Li atoms.

Heating of the samples at temperatures above T_D leads to out-diffusion of lithium as indicated by the decrease of the dark conductivity. The results of the thermal effusion measurements in Fig.3 show that Li effuses in a broad temperature range mainly as LiOH which is probably formed after out-diffusion by reacting with residual water in the system. Also small bursts of Li and LiH were observed. The onset of the LiOH effusion at $T \approx 150$°C indicates the start of macroscopic Li diffusion in the film. At about 420°C the out-diffusion of Li reaches a maximum. At higher temperature the normal H_2 effusion takes place which is known to lead to irreversible changes of the structure and to the formation of voids. They probably act as effective internal Li sinks and reduce the Li out-diffusion via the surface.

To test the importance of internal voids for the Li diffusion we diffused Li at T_D=230°C into pre-annealed films (T_A=500°C and 600°C, respectively). The pre-annealing removed most of the hydrogen. After in-diffusion again a strongly altered dielectric response was observed by spectroscopic ellipsometry, indicating

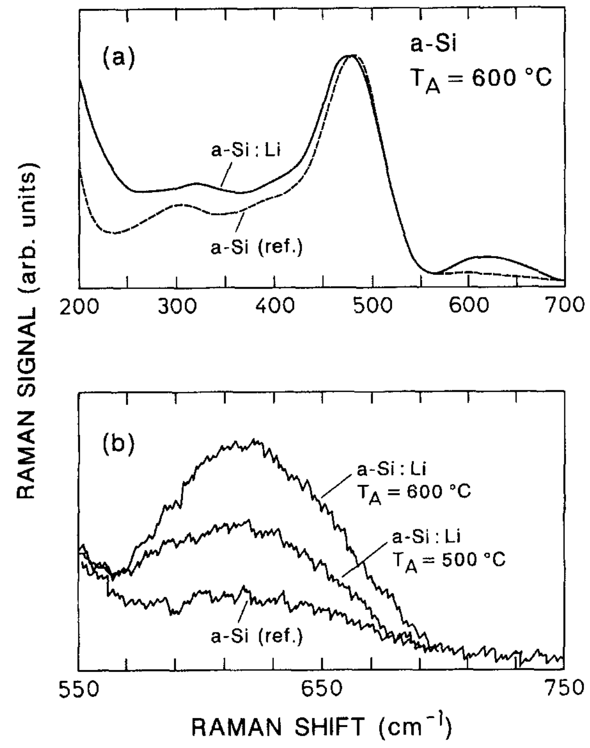

Fig. 4: Raman scattering spectra of a pre-annealed (T_A=600°C) reference film and two Li-doped films (pre-annealed at T_A=500°C and 600°C, respectively).

again the occurance of a large concentration of Li clusters. In addition, several new features were seen in the Raman spectra of these dehydrogenated samples.

The normalized Raman spectra of a Li-doped and a reference sample (both were pre-annealed at the same temperature, T_A=600°C) are compared in Fig.4a. The spectrum of the a-Si:Li film shows a relative increase of the Raman scattering at frequencies below 400 cm^{-1} (LO and LA phonon regime) and a broadening of the TO-phonon peak at 480 cm^{-1}. These changes indicate a strong decrease of the Si-network order due to Li precipitation. They also show that up to this pre-annealing temperature no crystallization took place.

A second interesting observation is a new broad Raman peak at frequencies around 620 cm^{-1} which rises with increasing T_A as shown in Fig.4b. We attribute this absorption to a SiLi alloy which is correlated with the increasing Li precipitation. Observation of this peak is difficult in hydrogenated samples because there is an overlap with the Si-H bending modes at 630 cm^{-1}.

It is also interesting to note that these dehydrogenated, Li-diffused films show a strong enhancement of the Raman scattering efficency (by a factor of about two) which can be related to the change of the dielectric function at the Raman laser frequency. This effect will be discussed in more detail elsewhere.

The present data show that lithium in Li-diffused a-Si:H films occurs in a number of different configurations. New vibrational modes suggest the formation of LiH and most likely LiOH in the near surface layer. A reaction with interstitial oxygen or oxydized interfaces possibly leads to Li_xO complexes. In addition, strong changes of the dielectric function confirm that metallic Li precipitates in clusters. The results suggest a decrease of the cluster size with increasing diffusion temperature. In the dehydrogenated films voids act as effective precipitation centers, and increasing accumulation of Li produces structural changes of the Si network. This is connected with an alloying of Si and Li as indicated by a new Raman mode attributed to SiLi vibrations.

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