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Hydrogen related effects in a-Si:H studied by photothermal deflection spectroscopy

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ABSTRACT

A study of thermal annealing of a-Si:H samples between 300°C and 600°C has been carried out. At increasing annealing temperatures, the sub-gap measured by PDS increases showing two inflections, centered at 375°C and 550°C. The hydrogen content measured by thermal desorption spectroscopy evolves in the same temperature range, whereas the evolution of the hydrogen content deduced from the ir transmission spectra differ, decreasing sooner and vanishing already at about 450°C.

Introduction

Hydrogen plays an important role in the properties of hydrogenated amorphous silicon (a-Si:H). Phillips [1] first pointed out that an amorphous structure with coordination 4, like Si, only exists with some amounth of non fully coordinated atoms, namely dangling bonds. In such a way, evaporated amorphous silicon presents a defect density of 10^{19} cm^{-3} [2]. Hydrogen saturates the dangling bonds and reduces three orders of magnitude the defect density, down to 10^{16} cm^{-3}.

Hydrogen acts as a softener of the stress of Si network, influencing the structure of the material and the defects in the gap and band tails.

When an a-Si:H sample is annealed at increasing temperatures, hydrogen is progressively removed and the properties of the material change as a consequence of hydrogen diffusion and eventual Si network restructuration.

In the present paper, a systematic study of the properties of a-Si:H after removal of hydrogen by annealing at temperatures between 300° and 600°C is presented. Vibrational properties are studied by ir transmission spectroscopy (IRS), sub-gap absorption is studied by photothermal deflection spectroscopy (PDS) and the hydrogen evolved is studied by thermal desorption spectroscopy (TDS).

Experimental

The samples were obtained by depositing 2 µm of device quality a-Si:H on Corning 7059 glass and crystalline silicon by rf (13.56 MHz) glow discharge decomposition of pure silane. The rf power, the substrate temperature and the gas pressure were kept at their optimum values (5W, 300°C, 250 mTorr) for our r.f. reactor. The sample show a defects density of 1.08×10^{16} cm^{-3} and an Urbach energy of 55 meV, values reported in the literature for high quality films.

Annealings are done in a quartz tube under high vacuum (typically 10^{-6} mbar). The tube is long enough to be heated in one side without heat the other side. When the warm side has reached the prefixed temperature the sample is thrown down the tube. The annealing time is of two hours. The cooling time

depends of annealing temperature, being more or less one hour.

The TDS system is constituted by a quadrupolar mass spectrometer (Dataquad, Spectramass) connected to a personal computer (PC) to collect the values of the effused hydrogen flux. The temperature ramp, with 0.33ºC/s slope, is controlled by the PC trough a Phillips Controller KS 4580. The integration of the effusion spectrum provides the total hydrogen content of the sample once knowing the sample thickness and area, and having calibrated the hydrogen flux [3].

The ir spectra of samples has been performed in a Nicolet 5ZDX-FT IR Spectrometer, in the range 4000-400 cm^{-1}. Once removed the interferences, the hydrogen content has been deduced from wagging peak absorption (centered at 640 cm^{-1}) [4] using the Brosdky method [5].

For several years PDS has been applied to study the optical absorption behaviour of a-Si:H thin films. The extreme sensitivity of PDS makes it ideal for examining low levels of absorption in thin films. The typical transverse PDS setup used in our experiments consist in an halogen lamp, a PTI 01-002 monochromator, and a SR540 mechanical chopper were used in the pump beam unit. A SR530 lock-in amplifier was connected to a position sensor to measure the deflection of He-Ne laser probe beam. The samples were put in a quartz cell filled with CCl_4. A personal computer controls the monochromator, changes the order filters and stores the PDS signal read from the lock-in amplifier.

From the PDS signal, the energy dependence of absorption coefficient is obtained by means of incoherent approximation [6]. The Urbach edge width and the sub band gap absorption were measured using PDS, and the subgap density states (DOS) were obtained following the procedure of Jackson [7].

Results

The absorption spectra deduced from PDS measurements corresponding to intrinsic a-Si:H annealed at different temperatures are shown in Figure 1. It can be readily seen that the annealing temperature enhances gap-state absorption and the Urbach edge width. No significant change in the absorption spectra is observed at annealing temperatures below 350 °C. As

the annealing temperature (Ta) is raised to 500°C, subgap absorption increases dramatically, while the exponential absorption region shifts to lower energies.

Figure 2 shows the variation of the Urbach energy Eo and the defect density Ns versus the annealing temperature. In amorphous semiconductors, the Urbach edge parameter is coupled to the lattice disorder [8]. It can be seen that the Urbach tail broadens and shifts to lower energies, interpreted as an increase in the disorder along with the hydrogen effusion. Also it can be observed the increase of the defects density along with the annealing temperature.

In Figure 3 are represented the evolution of the film hydrogen content deduced from ir transmission spectra according to the annealing temperature (a), the remaining hydrogen content measured from TDS as a function of temperature from an as-deposited sample (b) and an annealed sample at 500°C (c). These two types of evolution do not match, the IR evolution vanisching at lower temperature than the TDS one.

Discussion

The PDS results shown in figure 2, put in evidence that the change in sub-gap absorption of the annealed samples have a non-monotone behaviour, two inflections in the defect density appear at different annealing temperatures, a low temperature inflection at 375°C and a high temperature inflection at 550°C. This behaviour could be explained by the hydrogen effusion at low and high temperature.

The results of hydrogen content measured by IRS and TDS are in apparent disagreement that can be observed by comparing Fig. 3 (a) with (b). This arises from the difference between the dynamic annealing of TDS and the two hours annealing used for IRS measurements. This contradiction disappears by considering the hydrogen content measured by TDS for a sample annealed at 500°C during two hours, that is in good agreement with the IRS result and which stands out the influence of the annealing time.

By comparing the PDS results (Fig. 2) with the evolution of hydrogen content measured from ir spectra (Fig. 3), a surprising discrepancy is observed. At a temperature of 500°C, when only a little change in sub-gap absorption is observed, the hydrogen

content detected by IRS is reduced in a portion of 90% with respect to the as-deposited state. From these figures it also appears that the dangling bonds and hydrogen do not evolve parallely. In effect at the lower temperatures the hydrogen evolution is much faster than the associated dangling bond evolution (from Si-H rupture), while at the higher temperatures the dangling bond evolution increases drastically. This difference of behaviour between dangling bonds and hydrogen through annealing can appear consequent if dangling bond reconstruction is taken into account. One of the parameters governing the dangling bond reconstruction may be their mean distance. Thus one of the considerations to account with is hydrogen clustering. In effect, at the lower temperatures the hydrogen evolution proceeds essentially from clustered hydrogen, thus the dangling bonds created have a small mean separation which allons their reconstruction through Si-Si bonding. Instead, at higher temperatures the envolving hydrogen proceeds essencially from isolated Si-H bonds, leading thus to isolated dangling bonds which reconstruction is hence difficulted, and hence the drastic dangling bond evolution observed at the higher temperatures.

Conclusion

The defects density upon annealing presents a non monotone behaviour with two inflections centered at 375°C and 550°C, that could be attributed to low and high hydrogen evolution respectively.

A given amount of effused hydrogen produces a much small proportion of dangling bonds when proceeding from low temperature annealings than from higher temperatures.

This can be attributed in part to hydrogen evolution from clustered hydrogen in the first case, leading thus to clustered dangling bonds of easy reconstruction through Si-Si bonding, and to isolated hydrogen in the second case, making dangling bond reconstruction less easy since being isolated.

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Figure Captions

Figure 1. PDS deduced absorption spectra of intrinsic a-Si:H after annealing at different temperature.

Figure 2. Energy of Urbach edge, Eo, and defects density, Ns, as a function of the annealing temperature.

Figure 3. a) H content from IRS versus anealing temperature. b) Thermal evolution of H content from TDS for as-deposited sample and c) for 500°C annealed sample.

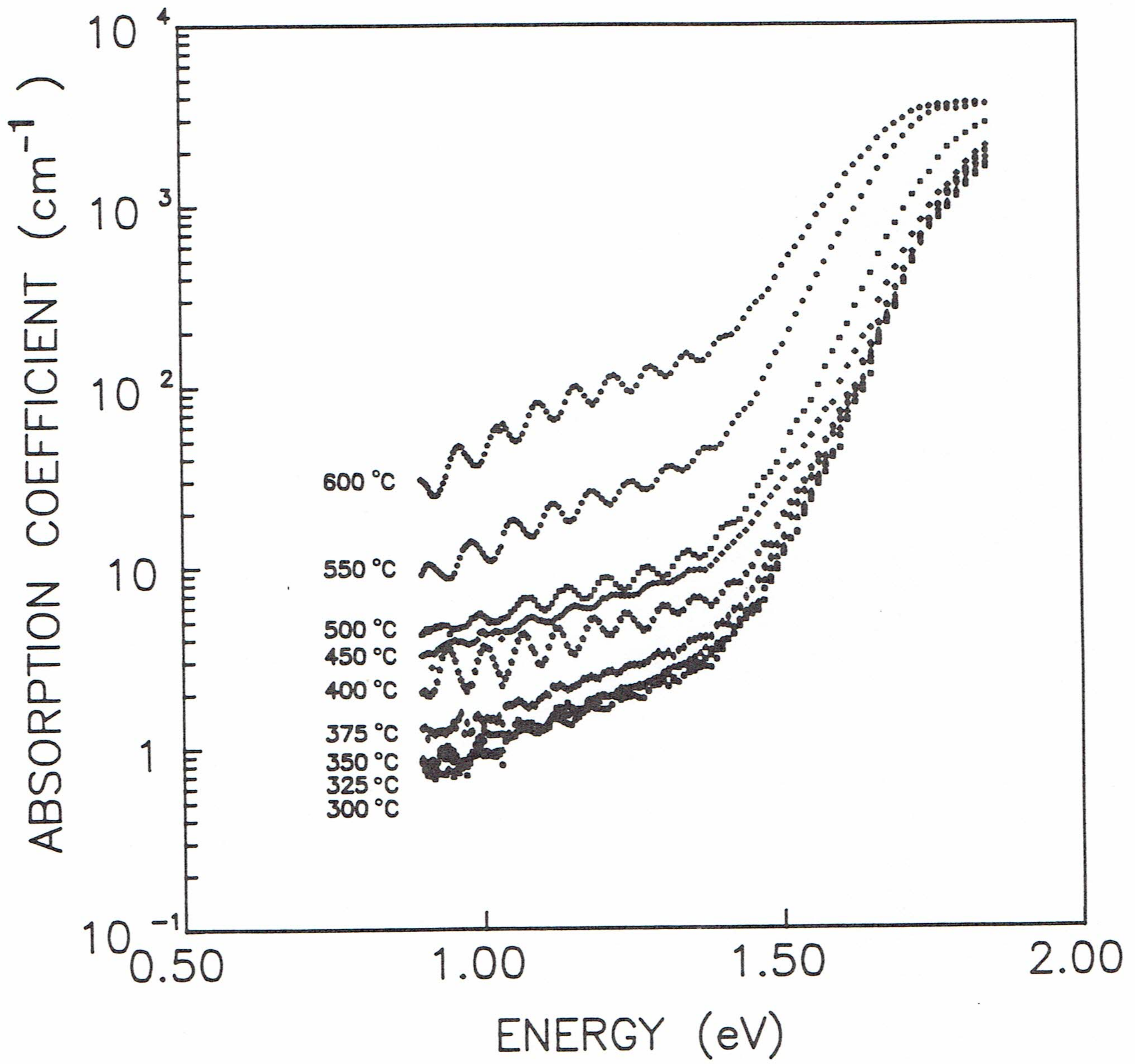

Fig. 1

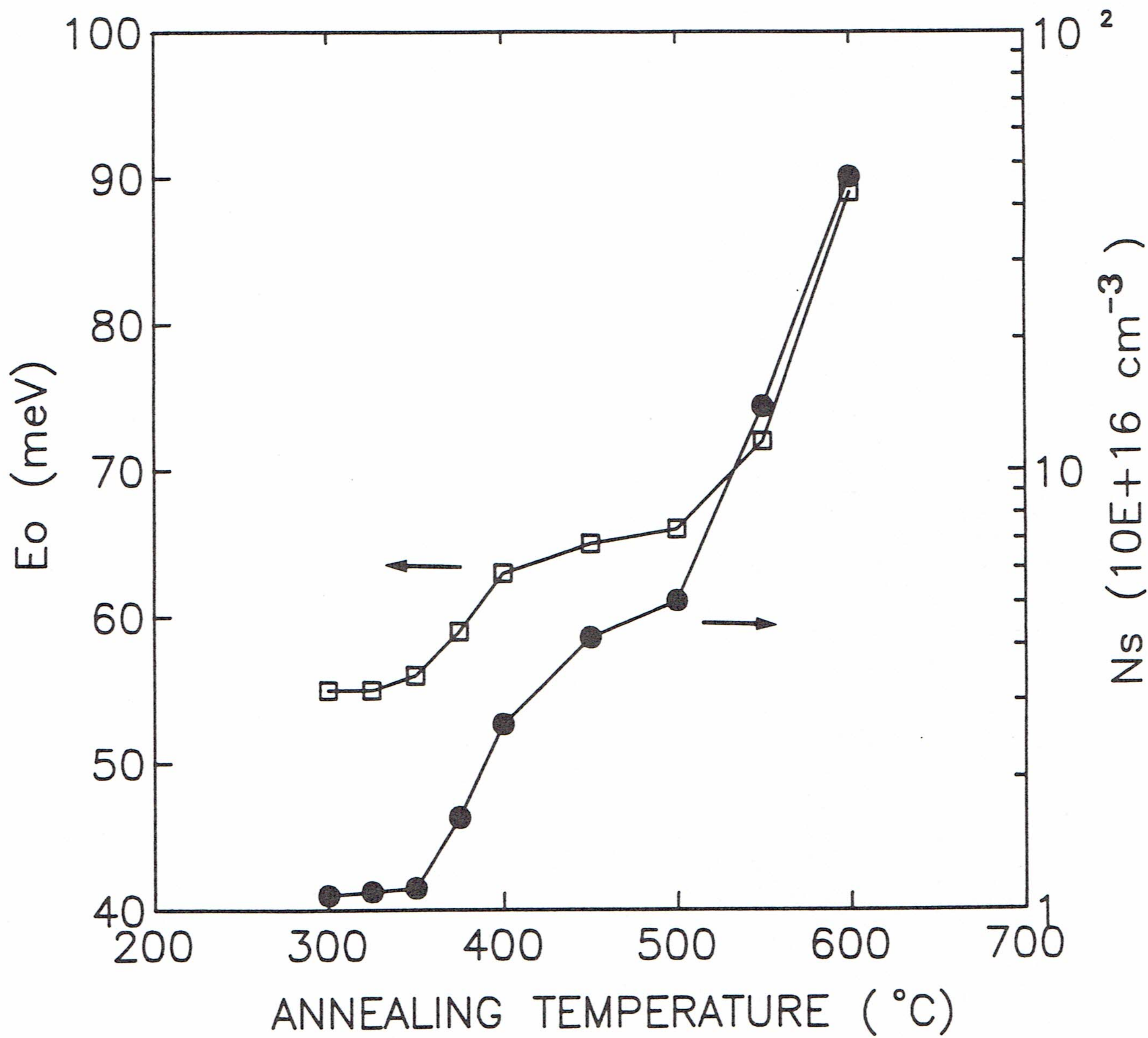

Fig. 2

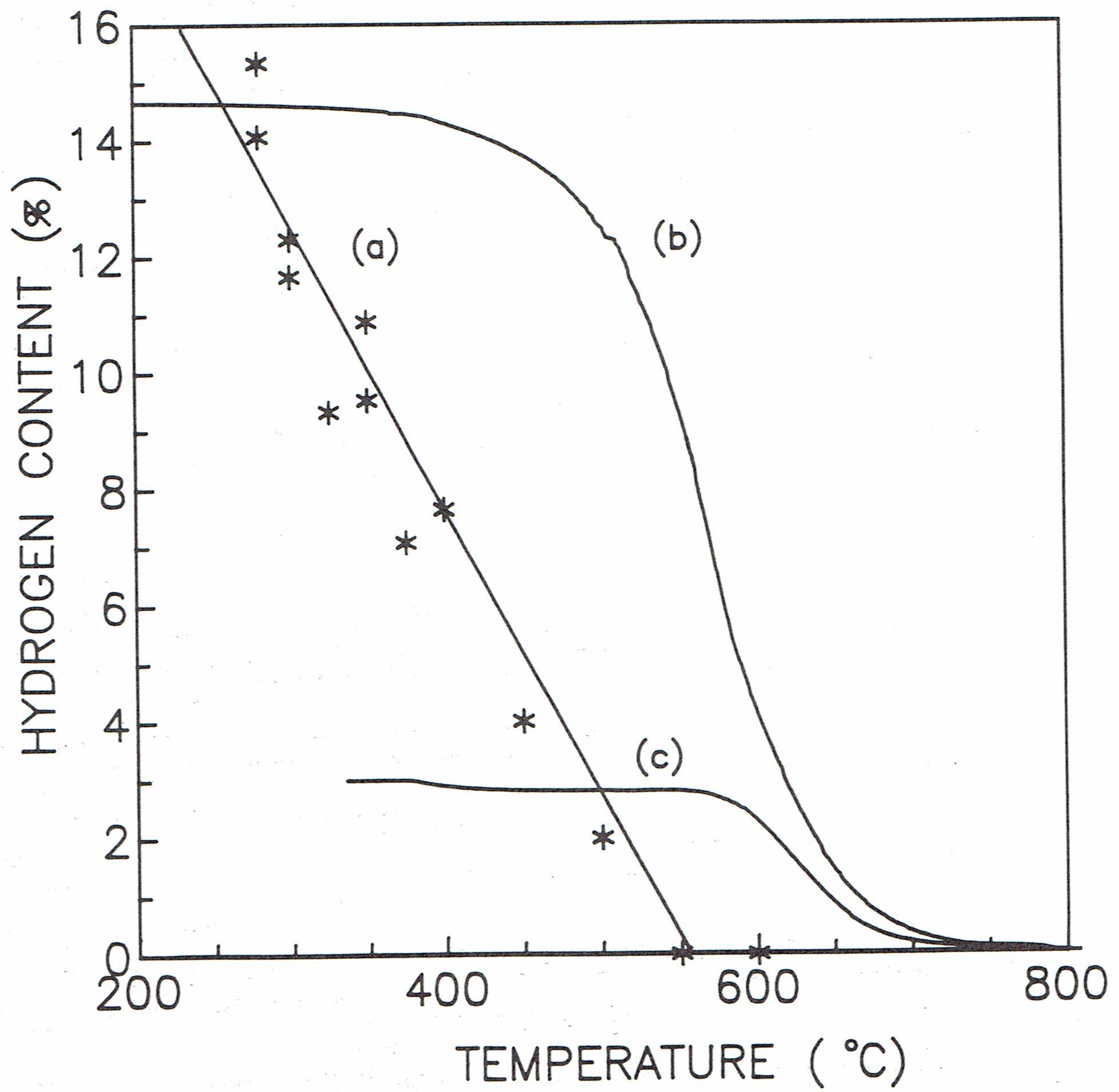

Fig. 3