OPTO-ELECTRONICS REVIEW **8**(4), 385–387 (2000)

Formation and relaxation of metastable defects in amorphous silicon

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We studied relaxation of defects formed during fast quenching in low pressure chemical vapour deposition (LPCVD) amorphous silicon with different hydrogen concentrations (from 0.05 at.% to 15 at.%) doped with boron or phosphorous (2 at.%). Results of measurement of dark conductivity after quenching and slow cooling as well as measurement of the isothermal relaxation of dark conductivity after quenching in different temperatures are presented. We found relaxation time higher in P-doped than in B-doped films in the same annealing temperature. Activation energy of relaxation time was independent on hydrogen concentration and was higher for B-doped samples.

Keywords: amorphous silicon, metastability, relaxation, hydrogen.

1. Introduction

Hydrogen plays a substantial role in determining the properties of hydrogenated amorphous silicon films. In glow discharge deposited films a-Si:H, it makes doping possible by passivating large number of dangling bond defects caused by bonding disorder. At the same time, various metastable phenomena such as thermal and light induced metastabilities observed in a-Si:H films have also been connected with the movement of hydrogen in these films [1,2]. Also, the type and magnitude of metastable changes also depend on the dopant, such as phosphorous or boron. In doped, hydrogenated amorphous silicon two different phenomena coexist: the reversible increase in dangling-bond density and the reversible increase of doping efficiency. These effects depend on the type of excitation applied to a film (light soaking, rapid cooling, or bias) and on the doping level and the type of dopant. Therefore, it is important to study influence of hydrogen and dopants on metastability in amorphous silicon to understand the causes of metastable phenomena.

We investigated relaxation of metastable defects in doped (P or B) LPCVD a-Si films as a function of hydrogen concentration, C_H, and temperature. This variation of C_H over 2 orders of magnitude helped us examine the role of hydrogen and dopants in relaxation phenomenon.

2. Experimental

LPCVD a-Si films have been prepared by thermal decomposition of 100% silane at 560°C. In undoped films, C_H was 0.06 at.% (SIMS) and the spin density was 10^{19} cm^{-3} (ESR). The films (0.5 μm thick) were implanted with B or P concentration of 10^{21} atoms/cm^3 (2 at.%), followed by implantation with H doses corresponding to the range of 0.05–15 at.%. Ion implantation was done at three energies 25, 40, and 60 keV to ensure uniform distribution. Further, the films were annealed at 400°C for 20 h in nitrogen atmosphere. The conductivity measurements were done in coplanar geometry. Dark conductivity versus reciprocal temperature was measured at a temperature range of 300–450 K, with a heating rate of 1.5 K/min. The metastable changes in a-Si:H were induced by quenching from 675 K to liquid nitrogen temperature. The details of conductivity measurements and rapid cooling are described elsewhere [3].

3. Results

The room temperature dark conductivity, σ_{300}, for low hydrogenated films (0.05 at.%) is the same for boron and phosphorous doped films and equals 1×10^{-2} Ω^{-1}cm^{-1}. The room temperature dark conductivity decreases with increase in hydrogen content for both dopant types. σ_{300} for highly hydrogenated (12 at.% H) B-doped films is 7×10^{-4} Ω^{-1}cm^{-1} and for the same C_H, P-doped films is 2×10^{-4} Ω^{-1}cm^{-1}. At the same time, activation energy increases. Decrease in σ_{300} with increasing hydrogen content means that hydrogen introduction decreases doping efficiency.

The room temperature dark conductivity measured after quenching is higher than after slow cooling. Magnitudes of these changes depend on hydrogen content and type of dopant (B or P) [4]. The ratio of the room-temperature dark conductivity after quenching and slow cooling increases to 2.8 and 2.2 for P- and B-doped films for C_H around 7 at.%,

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respectively. Decrease in this ratio is observed when C_H further increases. Dark conductivity is thermally activated with the activation energy E_A. Activation energy of slow cooled films increases with increase in hydrogen content from 0.22 eV (both dopant types) for low hydrogenated films to 0.33 eV and 0.29 eV (15 at.% of C_H) for P- and B-doped films, respectively. E_A measured after quenching is lower than after slow cooling. Difference between E_A, after slow cooling and quenching, is around 10 meV for low hydrogen content and increases to 20 meV (B-doped) and 30 meV (P-doped) with increasing C_H up to 7 at.%. Further increase in hydrogen content causes decrease in this difference.

Room temperature dark conductivity versus activation energy is shown in Fig. 1. Logarithm of σ_{300} decreases with increasing E_A, independently on a type of dopant and kind of cooling. σ_{300} is 2×10^{-2} $\Omega^{-1}cm^{-1}$ for activation energy 0.19 eV and with increasing E_A up to 0.33 eV decreases to 2×10^{-4} $\Omega^{-1}cm^{-1}$.

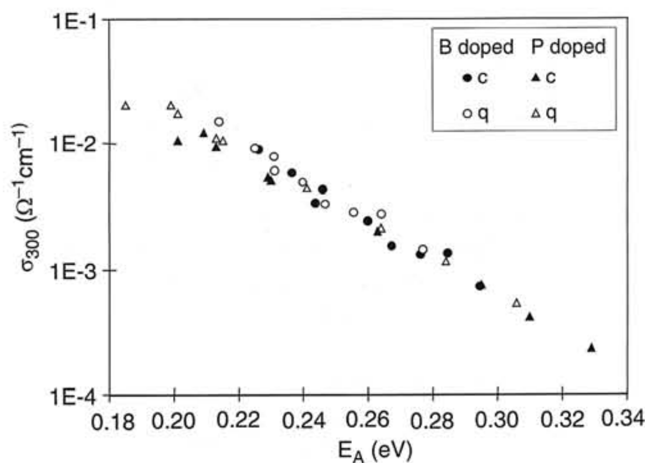

Fig. 1. The room temperature dark conductivity, σ_{300}, after slow cooling and quenching versus activation energy, E_A, for phosphorous- and boron-doped films.

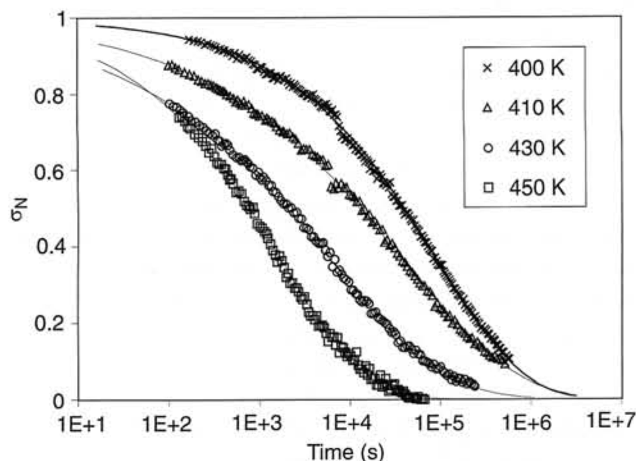

Fig. 2. Example of time characteristics of normalised dark conductivity after quenching in different annealing temperatures (B doped sample, hydrogen concentration 0.5 at.%).

We investigated time dependence (up to 250 h) of the isothermal relaxation of the dark conductivity after fast quenching at different annealing temperatures (between 400 and 500 K) for the films with the different C_H. Dark conductivity, measured after quenching in the constant temperature, slowly relaxes to the value measured after slow cooling (example of such a characteristic is shown in Fig. 2). Normalised conductivity

$$\sigma_N(t) = \frac{\sigma(t) - \sigma(\infty)}{\sigma(0) - \sigma(\infty)} \tag{1}$$

where $\sigma(0)$ and $\sigma(\infty)$ are the conductivity values in the quenched state at t = 0 and in slow cooled state, respectively. Normalised conductivity follows a stretched exponential

$$\sigma_N(t) = \exp\left\{-\left(\frac{t}{\tau}\right)^{\beta}\right\} \tag{2}$$

where τ is the relaxation time and β is the dispersion parameter.

The results of relaxation measurement were fitted to this expression (solid line in Fig. 2). The relaxation time τ, is plotted as a function of inverse temperature for different hydrogen concentrations in Fig. 3. The relaxation time τ, decreases of almost two orders of magnitude with an increase in annealing temperature from 410 K to 490 K or from 400 K to 450 K, for P- and B-doped films, respectively. At a constant annealing temperature (Fig. 4), the relaxation time is longer for P-doped films. For example, at an annealing temperature of 450 K, τ is in the of range 10^4–10^6 s for P-doped and 6×10^2–2×10^3 s for B-doped films. Inversion of the relaxation time τ^{-1} is thermally activated with activation energy E_τ = 0.9–1 eV for phosphorous-doped and E_τ = 1.25–1.3 eV for boron-doped films. E_t is higher for P-doped than for B-doped films about 0.3 eV.

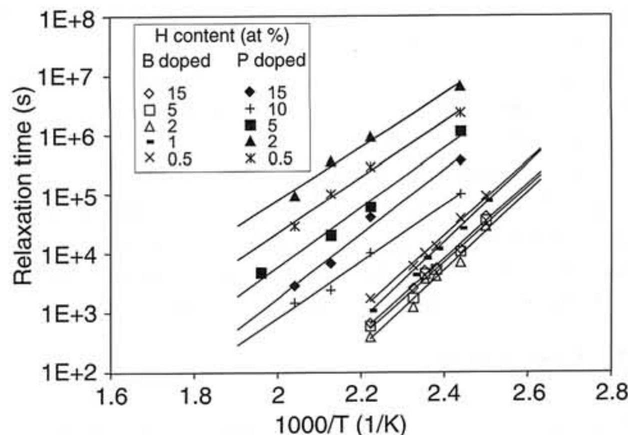

Fig. 3. Relaxation time, τ, versus inverse annealing temperature for boron and phosphorous doped films with different hydrogen content.

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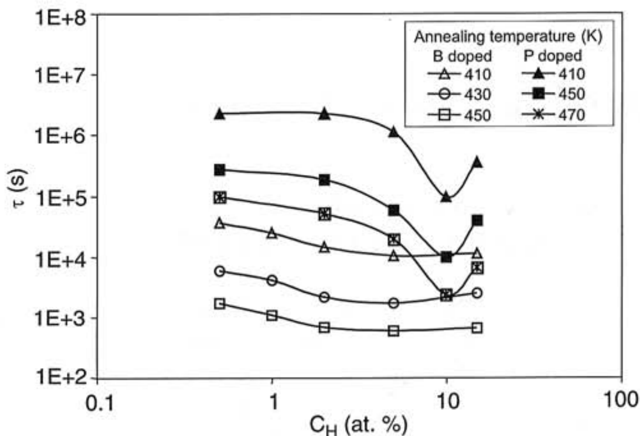

Fig. 4. Relaxation time, τ, versus hydrogen concentration for different annealing temperatures.

We suggest that it can be explained by dopant passivation mechamism proposed by Jackson [5]. He proposed that doping is determined by equilibration between passivated and unpassivated fourfold dopants. The relative doping efficiency of the fourfold sites is determined by passivation of activated dopants through the presence of hydrogen. Quenching increases number of active dopants than metastable increases doping efficiency. Jackson has shown that P is passivated with larger activation barrier than B [5]. It agrees with difference in activation energy of relaxation time in our films.

4. Conclusions

In conclusion, we found that at the same annealing temperature for the same hydrogen content, relaxation time is longer in phosphorous-doped than in boron-doped films. Activation energy of relaxation time is almost the same for the films with different hydrogen content with one type of dopant. E_τ is larger in B-doped films than in P-doped films. This suggests the existence of a larger barrier for hydrogen diffusion in B-doped films and better stability of these films.

Acknowledgements

This work was sponsored by the State Committee for Scientific Research (KBN), Warsaw, Poland project 8T11B01516 and the Second Polish-American Fund Maria Skłodowska-Curie, grant no MEN/DOE-98-345.

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