Paper

Metastability problems in amorphous silicon

Stanisław M. Pietruszko and Marek Kostana

Abstract — The results of study of the influence of boron and phosphorous doping and hydrogen content on transport properties and thermally induced metastability of LPCVD a-Si are reported. The thermally induced metastability has been observed in both unhydrogenated and hydrogenated P-doped a-Si films. Metastability is a barrier for wide application of a-Si such solar cells. In this paper we report our studies on the effect of thermally induced metastability in LPCVD a-Si as a function of implanted boron and phosphorous concentration. We have investigated films unhydrogenated and hydrogenated by ion implantation. The results are qualitatively agreed with bond breaking model.

Keywords — amorphous silicon, metastability, thermal quenching.

1. Introduction

Amorphous silicon and its alloys, due to their physical properties and their manufacturability, have attracted rapidly growing interest in the recent years. A major advantage of amorphous over crystalline technology is dramatically reduced cost so low that some consumer applications like solar cells, thin film transistors, etc. Solar cells are applied in telecommunication for supply electricity for base stations far away from electric grid. However, the performance of a-Si-based devices is limited by reversible, metastable changes induced by light, high-energy particles, carrier injection, the accumulation of carriers at a-Si interfaces, and thermal quenching [1]. All of these effects are reversible by annealing to a sufficiently high temperature, and all are believed to be caused by the same degradation mechanism [2].

Since the discovery of metastable effects in a-Si:H, there is strong circumstantial evidence for the role of hydrogen and dopants, although complete proof is still lacking. The evidence stems primarily from the observation of hydrogen motion at the same temperature as the metastability effects. The activation energy of defect annealing is comparable with that of hydrogen diffusion. Furthermore, the doping trends are the same – dopants which result in a large hydrogen diffusion coefficient also lead to faster defect relaxation. In the other hand hydrogen makes doping possible by passivating large number of dangling bond defects caused by bonding disorder.

Kind and magnitude of metastable changes is dependent on both hydrogen and dopant such phosphorous or boron. In doped hydrogenated amorphous silicon, there are coexistence of two different phenomena: the reversible increase of dangling bonds density and the reversible increase of doping efficiency. These effects depend on the kind 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 reasons of metastable phenomena.

There are several barriers to the study of metastability in low-hydrogen-concentration a-Si. Most a-Si is grown from hydrogen-bearing precursor gases, and hydrogen content is difficult to reduce to below a few atomic percent. Implantation of hydrogen to LPCVD a-Si films with very low hydrogen content (0.06 at.% H) allowed us to investigate films with low and high hydrogen content. In this paper we report our studies of effect of rapid quenching in LPCVD a-Si unhydrogenated films and hydrogenated as a function of phosphorous concentration. Variation of P concentration over five orders of magnitude with different hydrogen contents help us examine the role of dopant in metastability phenomenon.

2. Experimental

LPCVD a-Si films (0.5 μm thick) are grown on oxidised crystalline silicon substrate at 560°C. As-grown, undoped films contain ~ 0.06 at.% hydrogen (SIMS) and spin density is 10^{19} cm^{-3} (ESR). These films are phosphorous or boron doped by ion implantation (different doses from 10^{11} to 10^{17} ions/cm^2 at 150 keV). The average doping concentration, given by the ratio of the implanted dose to the amorphous film thickness, is from $2 \cdot 10^{15}$ to $2 \cdot 10^{21}$ cm^{-3}. One set of films was further implanted with hydrogen doses corresponding to 12 at.% of hydrogen content. Ion implantation was done at three energies 25, 40, 60 keV to ensure uniform distribution. Further, films were annealed at 400°C for 20 hours in nitrogen atmosphere. It was possible since FTIR measurements showed, that hydrogen starts effuse from these samples only after annealing at 425°C for 2 hours. The slow cooling and quenching were done after annealing for one hour at 400°C. The conductivity measurements are done in coplanar geometry using aluminium electrodes 0.1 mm apart. Dark conductivity versus reciprocal temperature is measured from 300 to 590 K with a heating rate of 1.5 K/min. More details about conductivity measurements and quenching are given elsewhere [3]. The activation energies, E_A were determined from the slope of the least square fit of the data to $\sigma = \sigma_0 \exp(-E_A/kT)$.

3. Results

Figures 1 and 2 show the logarithm of conductivity versus reciprocal temperature (1000/T) of hydrogenated a-Si films

(12 at.%) with different boron and phosphorous concentrations after slow cooling (filled points) and quenching (open points). The curves shifted for clarity. The metastability effect and its dependence on dopants doses can be clearly seen.

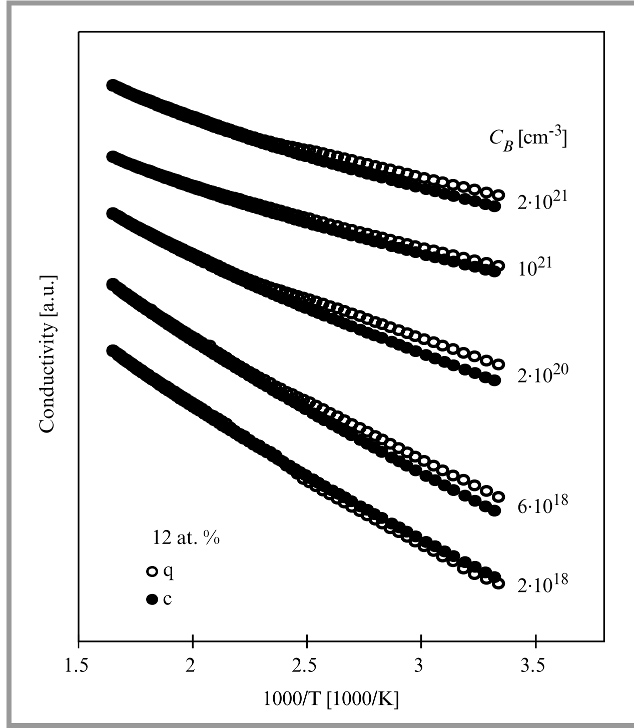

Fig. 1. The logarithm of conductivity versus reciprocal temperature of hydrogenated a-Si films (12 at.%) with different boron concentration after slow cooling (filled points) and quenching (open points). The curves shifted for clarity.

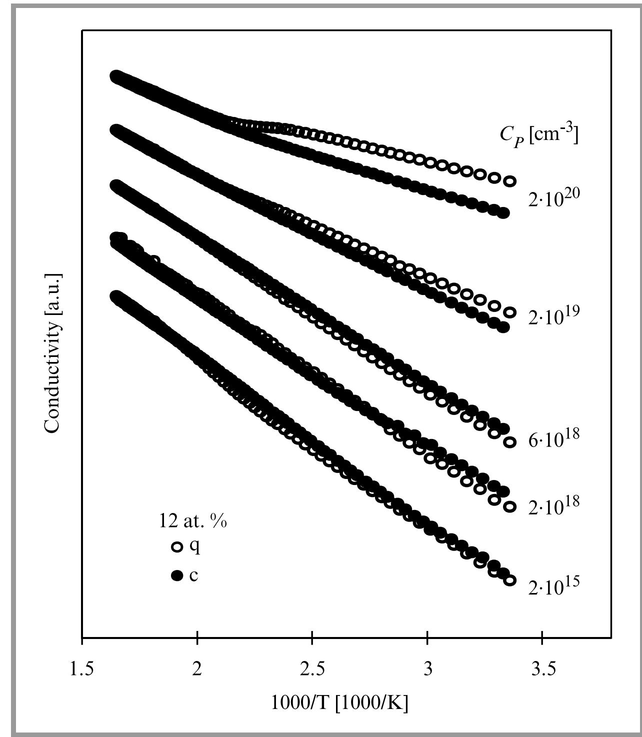

Fig. 2. The logarithm of conductivity versus reciprocal temperature of hydrogenated a-Si films (12 at.%) with different phosphorous concentration after slow cooling (filled points) and quenching (open points). The curves shifted for clarity.

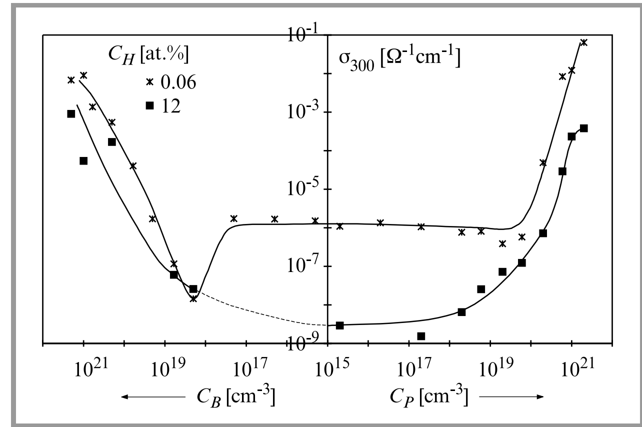

Fig. 3. The room temperature dark conductivity, σ_{300} versus phosphorous and boron concentration of unhydrogenated and hydrogenated (12 at.%) a-Si films.

The room temperature dark conductivity, σ_{300}, of as-grown films (0.06 at.% H) is about $1\cdot10^{-6}\Omega^{-1}\text{cm}^{-1}$ (Fig. 3) and remains constant up to phosphorous concentration $6\cdot10^{19}$ cm^{-3}, then increases to $8\cdot10^{-2}$ for the highest P concentration ($2\cdot10^{21}$ cm^{-3}). In the case of boron doped films σ_{300} remains constant up to boron concentration $2\cdot10^{17}$ cm^{-3} then decrease to $10^{-8}\Omega^{-1}$ cm^{-1} for $C_B = 2\cdot10^{18}$ cm^{-3} and further increase to $10^{-2}\Omega^{-1}$ cm^{-1} for highest boron concentration ($2\cdot10^{21}$ cm^{-3}). Since σ_{300} begins increasing for phosphorous and boron concentration which is approximately equal to the measured spin density of 10^{19} cm^{-3}, we suggest that dopants passivates dangling bonds in unhydrogenated material. When most of them are passivated, phosphorous or boron atoms become active dopant. Existence of minimum of conductivity for $C_B = 2\cdot10^{18}$ cm^{-3} suggest that in such doped films Fermi level is located in half of mobility gap. In the case of hydrogenated (C_H = 12 at.%) films, room temperature dark conductivity $3\cdot10^{-9}$ for lowest concentration of phosphorous slowly increases to $10^{-2}\Omega^{-1}$ cm^{-1} for the highest P concentration. Similarly for B doped films σ_{300} increase from $2\cdot10^{-8}\Omega^{-1}$ cm^{-1} to $10^{-3}\Omega^{-1}$ cm^{-1} with increasing of C_B in the range of $2\cdot10^{18}\div2\cdot10^{21}$ cm^{-3}, but we do not know how it changes for low boron concentration (up to $2\cdot10^{18}$). Significant difference in room temperature conductivity between films unhydrogenated and hydrogenated films for same dopant concentration above $6\cdot10^{19}$ cm^{-3} suggests that hydrogen passivated dangling bonds of a-Si network, so the conductivity decreased to the level comparable with glow discharge a-Si films. We suggest that it can be connected with deactivation of dopants by hydrogen [3].

The activation energy, E_A is shown in Fig. 4. For unhydrogenated films, E_A is in order of 0.2 eV and remains constant up to P concentration of 10^{19} cm^{-3}, then it jumps to 0.6 eV for P concentration of $2 \cdot 10^{19}$ cm^{-3} (what corresponds to increase of σ_{RT300}), and decreases to 0.2 eV for the highest phosphorous concentration. In the case of boron doped films E_A change similarly but jump is smaller, from 0.2 eV to 0.35 eV for $C_B = 2 \cdot 10^{19}$ cm^{-3}. We suggest that there is change of mechanism of carrier transport at the room temperature for the dopant concentration higher that spin density in as-grown films (10^{19} cm^{-3}). For hydrogenated films is about 0.65 eV for lowest P concentration and remains constant up to $6 \cdot 10^{18}$ cm^{-3}, then activation energy E_A decreases to 0.25 eV for the highest P concentration. In the case of boron doped films E_A decrease from 0.6 eV to 0.27 eV with increasing of B concentration from $2 \cdot 10^{18}$ cm^{-3} up to $2 \cdot 10^{21}$ cm^{-3}. The dependence of the activation energy on dopant concentration is correlated with the dependence of the room temperature dark conductivity. Again, the suggested the passivation of dopants by hydrogen can be seen.

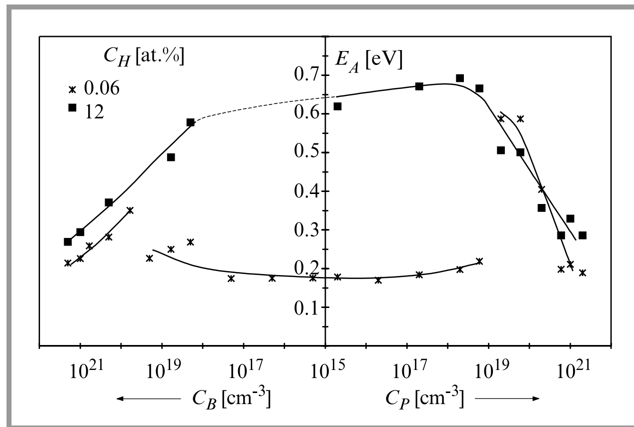

Fig. 4. The activation energy, E_A versus phosphorous and boron concentration of unhydrogenated and hydrogenated (12 at.%) a-Si.

The dependence of the ratio of room temperature conductivity after quenching, σ_{300q} and after slow cooling, σ_{300c} as a function of dopant content is shown in Fig. 5. In the case of unhydrogenated films the ratio of $\sigma_{300q}/\sigma_{300c}$ is about 1 up to P concentration $6 \cdot 10^{18}$ cm^{-3} and up to B concentration $2 \cdot 10^{19}$ cm^{-3}. Then increases to 2.4 and 2 for $C_P = 10^{20}$ cm^{-3} and $C_B = 10^{20}$ cm^{-3}, respectively. Further increasing of dopant concentration causes decreasing of the ratio of $\sigma_{300q}/\sigma_{300c}$. In the case of hydrogenated (12 at.%) films the ratio of $\sigma_{300q}/\sigma_{300c}$ is below 1 up to P concentration $6 \cdot 10^{18}$ cm^{-3} and up to B concentration $2 \cdot 10^{18}$ cm^{-3}. Then increases to 4 and 3 for $C_P = 10^{20}$ cm^{-3} and $C_B = 2 \cdot 10^{20}$ cm^{-3}, respectively. Further increasing of dopant concentration causes decreasing of the ratio of $\sigma_{300q}/\sigma_{300c}$.

Similar trends are observed in difference between the activation energy after slow cooling and quenching, ΔE_A (Fig. 6) which is between -30 and 0 meV up to $C_P = 2 \cdot 10^{-19}$ cm^{-3} and $C_B = 2 \cdot 10^{-19}$ cm^{-3}. Further increasing of dopant concentration causes increasing of ΔE_A to 40 meV and 20 meV for $C_P = 2 \cdot 10^{20}$ cm^{-3} and $C_B = 2 \cdot 10^{20}$ cm^{-3}, respectively. ΔE_A decrease for higher dopant concentration. In the case of hydrogenated (12 at.%) films in difference between the activation energy after slow cooling and quenching decrease from 60 meV to 10 meV and from 50 meV to 20 meV with increasing of C_P from $2 \cdot 10^{18}$ cm^{-3} to 10^{21} cm^{-3} and C_B from $2 \cdot 10^{20}$ cm^{-3} to 10^{21} cm^{-3}, respectively. Behavior of ΔE_A in these films with lower dopant concentration is not clear.

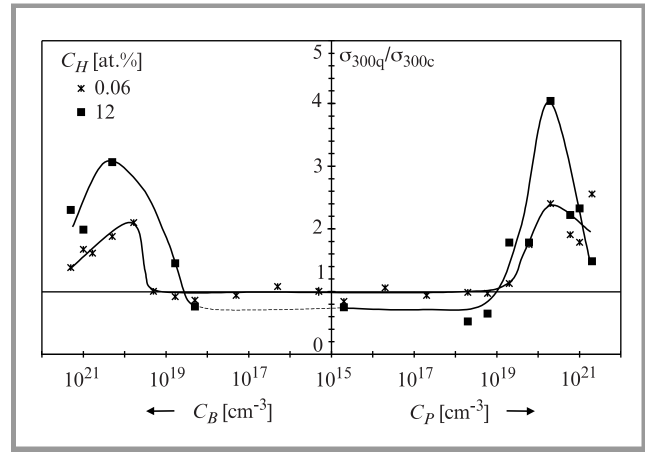

Fig. 5. The ratio of room temperature dark conductivity versus phosphorous and boron concentration of unhydrogenated and hydrogenated (12 at.%) a-Si films.

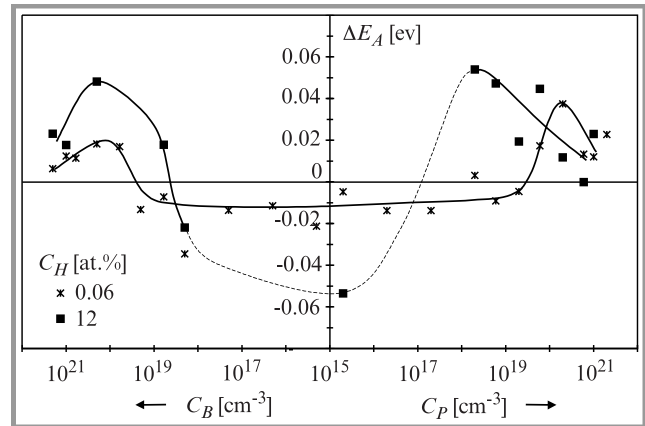

Fig. 6. Difference between the activation energy after slow cooling and quenching versus phosphorous and boron concentration of unhydrogenated and hydrogenated (12 at.%) a-Si films.

4. Conclusion

We have observed a reversible thermal induced metastable effect in LPCVD unhydrogenated and hydrogenated doped with different doses of phosphorous and boron amorphous silicon films. In unhydrogenated films metastable effects shows up above the concentration of dopant which is comparable to the spin density (10^{19} cm^{-3}) in as-grown films.

Quenching causes increase of room temperature dark conductivity and decrease of low temperature activation energy. Magnitude of these changes increases with hydrogen content. In hydrogenated films, the thermally induced metastability can be seen for the low P and B concentration range; quenching causes decrease of room temperature dark conductivity and increase of low temperature activation energy. For the higher P concentrations changes in both parameters are opposite and rapidly increase with phosphorous concentration.

These results qualitatively agree with bond breaking model [4]. In this model excitation (light, quenching) causes breaking of bond Si-H. If a nearest neighbour of such bond is weak bond Si-Si it can lead to produce new dangling bond, and macroscopically to increase of dangling bond density. If a nearest neighbour of Si-H bond is an inactive atom of dopant, breaking of such bond can cause activate of this atom, and macroscopically lead to metastable increasing of doping efficiency. There is coexistence of these two effects. Which effect dominates depends on concentration of hydrogen and dopants.

In our unhydrogenated films there is no metastability up to $2 \cdot 10^{19}$ cm^{-3} P concentration, but above this concentration dominate metastable increasing of doping efficiency. In hydrogenated films (12 at.%) up to P concentration $6 \cdot 10^{18}$ cm^{-3} and B concentration $2 \cdot 10^{18}$ cm^{-3} dominate creating of dangling bonds, then metastable increasing of doping efficiency. Decreasing of in difference between the activation energy after slow cooling and quenching and decreasing of the ratio of room temperature conductivity after quenching and after slow cooling with increasing of dopant concentration in highly doped films is difficult to explain and require further investigations.

Acknowlegment

This work was sponsored by the II Polish-American Fund Maria Sklodowska-Curie (grant no. MEN/DOE-98-345).

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