Technical Physics Letters, 2022, Vol. 48, No. 15

07.1;07.2;07.3

Influence of the conditions for the formation of $In_2O_3-SnO_2$ films by magnetron sputtering on the charge carriers lifetime in silicon

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Received July 1, 2021
Revised September 1, 2021
Accepted September 16, 2021

The critical influence of the indium-tin oxide films formation rate on the degradation degree of the a-Si:H/c-Si interface during magnetron sputtering is shown. It was found that when the distance between the magnetron and the sample is 10 cm, the lifetime decreases from ~ 2 ms to $10\,\mu$s, while when this distance is reduced to 7 cm, due to a two-times decrease in the deposition time, a decrease is observed from 1.5 ms to $450\,\mu$s.

Keywords: silicon, plasma-enhance deposition, thin films, passivation, ITO, solar cells.

DOI: 10.21883/TPL.2022.15.54271.18945

Silicon is the most common material on the basis of which semiconductor devices, including solar cells (SCs), are made. For most SCs, the characteristics are largely determined by recombination losses on defects. For example, the record value of the efficiency of silicon-based SCs 26.6% [1] belongs to the SCs based on the heterostructure a-Si:H/c-Si, where due to the effective passivation of the surface of crystalline silicon (c-Si) layer a-Si:H it is possible to achieve an extremely low rate of surface recombination. It should be noted that the thickness of the passivating layer a-Si:H should be as small as possible so as not to contribute to the series resistance, the same applies to the emitter layer, where part of the solar radiation is also absorbed. Usually the thickness of the layers a-Si:H on the silicon surface does not exceed 20 nm. At the same time, the bond strength of hydrogen atoms with silicon in the matrix a-Si:H is low, and subsequent external influences, such as heating to a temperature above 300°C, lead to the effusion of hydrogen from the layer a-Si:H, at the same time, the number of broken bonds at the heterogeneous boundary increases, leading to an increase in the recombination rate [2]. Another factor contributing to the degradation of the heterointerface may be plasma exposure, for example, during the formation of a transparent conductive coating, in particular In_2O_3-SnO_2 (ITO), over layer a-Si:H. It is known that during magnetron sputtering from oxide targets, the substrate is bombarded with high-energy particles, primarily negatively charged oxygen ions [3], which in the case of silicon can even lead to pinning of the Fermi level, as well as to a significant reduction in the lifetime of charge carriers (CCs) up to several microseconds [4,5]. At the same time, in some works it is noted that the subsequent annealing of the structure at temperatures of 180–200°C leads to the restoration of the CCs lifetime in silicon [4,5]. In others, on the contrary, data are given that annealing does not lead to the restoration of the values of the CCs lifetime to the initial level, but if the growth of ITO occurs at a substrate temperature in the range of 150–180°C, it is possible to avoid a sharp decrease in the lifetime of the CCs in silicon [6]. It was also shown that with a decrease in the thickness of the layers a-Si:H deposited on the surface of c-Si, the degree of damage to the heterointerface increases and at some critical value this change is irreversible, i.e. subsequent annealing does not restore the lifetime of [6]. However, studies on the influence of factors such as the distance from the magnetron to the sample, which can have a significant impact on the degree of degradation, are not given in the works. Therefore, the purpose of this work — to investigate the influence of the conditions of formation of ITO films by magnetron sputtering on the CCs? lifetime in silicon.

As the object of research, n-type silicon substrates with a resistivity of $5-10\,\Omega\cdot$cm and a lifetime of at least 3 ms were used. After removal of the natural oxide from the surface of c-Si in a solution of HF:H_2O, successive deposition of layers of unalloyed and phosphorus-doped a-Si:H was carried out on the back and front surfaces of silicon by PECVD at a temperature of 250°C. Details of deposition modes are provided in [7]. The total thickness of the deposited layers did not exceed 20 nm.

Next, the values of the effective CCs? lifetime in the manufactured structure were mapped by measuring the decay time of the photoluminescence signal [7]. In contrast to the method of measuring quasi-stationary photoconductivity, this method is suitable for the study of samples with dimensions less than 4 cm and gives a more complete picture of the distribution of the CCs? lifetime on the surface of the sample, and can also be used

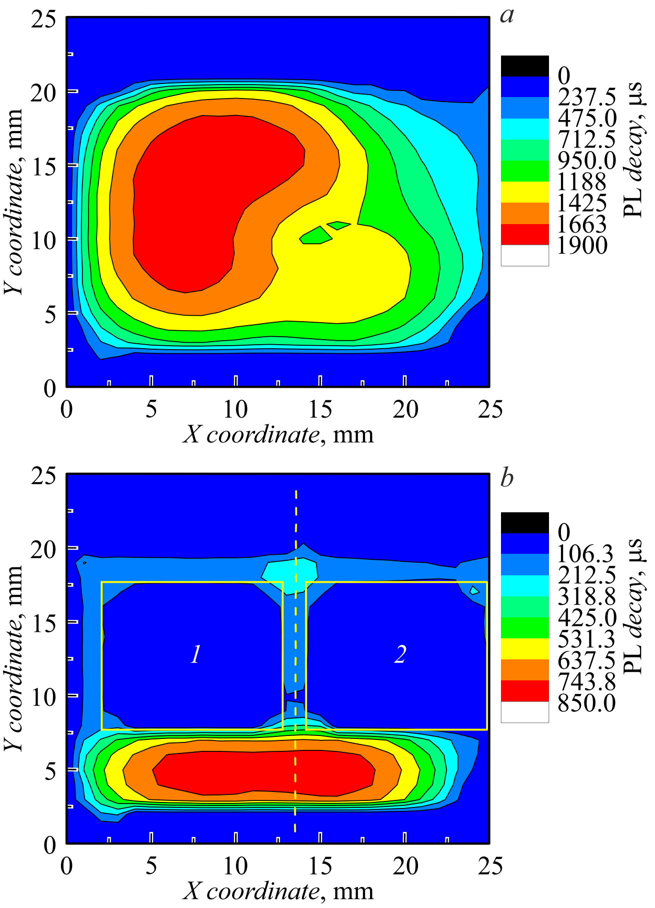

Figure 1. Map of the distribution of the CCs? lifetime before (*a*) and after (*b*) ITO deposition at a power of 50 W and a distance from the magnetron to the sample of 10 cm (*1* — without heating the substrate, *2* — heating to 130°C).

for measurements on samples with deposited transparent conductive layers.

To study the degradation of the sample to its surface through a rigid mask using the magnetron deposition method, the ITO layer was deposited on the Boc Edwards Auto 500 RF installation at an argon pressure of 0.2 Pa. At the same time, the magnetron power, the distance from the target to the sample and the sample temperature varied. The target was a 3″ disk of sintered oxide of the composition 90% In_2O_3 and 10% SnO_2 5 mm thick, manufactured by LTS Chemicals (USA). The thickness of the grown oxide in all experiments was 100 nm. After ITO deposition, the lifetime distribution over the sample surface was measured again. In some cases, after the measurements were carried out, the samples were annealed at a temperature of 130°C.

Fig. 1, *a* shows the distribution of the effective CCs? lifetime over the sample surface, measured immediately after deposition of layers *a*-Si : H. The maximum value of the lifetime is 1.9 ms, however, heterogeneity associated with edge effects is visible. Further, by covering various areas of the sample surface with a mask, ITO layers were deposited in various modes.

It is known that for different designs of magnetron sputtering plants, the optimal growth modes of ITO differ [8]. For this installation, the optimal growth mode at room temperature [9] was determined. It was shown that at a magnetron power of 50 W, a chamber pressure of 0.2 Pa and a distance from the sample to the magnetron of 10 cm an ITO layer with optimal characteristics is formed. However, after ITO deposition in this mode, a sharp decrease in the values of the effective CCs? lifetime was detected (up to 10 μs) (Fig. 1, *b*, region *1*). Annealing at a temperature of 130°C did not restore the lifetime.

According to the literature data, the heating of the substrate during growth should reduce the effect of plasma exposure by dynamic annealing of the resulting defects [6]. Repeated deposition of ITO was carried out on another site (area *2*) of the same sample, but at a temperature of 130°C. Again, a sharp decrease in the lifetime in silicon was found to 10 μs (Fig. 1, *b*).

After that, the distance from the magnetron to the substrate holder was reduced by 3 cm and ITO deposition was carried out again at a substrate temperature of 130°C. The remaining modes remained unchanged, while due to an increase in the growth rate, the film deposition time decreased by 2 times. It can be seen from Fig. 2 that after ITO deposition, the lifetime decreased from 1.5 ms to 450 μs. The obtained value significantly exceeds the values achieved earlier at a distance from the sample to the magnetron of 10 cm, and is acceptable for the manufacture of instrument-quality structures.

Note also that, despite the twofold increase in the growth rate, the film characteristics (transmission and resistivity) did not deteriorate, but on the contrary, improved their values: the transmission coefficient at a wavelength of 480 nm increased from 88 to 93%, and the resistivity decreased from $5.5 \cdot 10^{-4}$ to $3.5 \cdot 10^{-4}\,\Omega \cdot$ cm (when compared with a film grown without heating the substrate). The fact is that heating of the substrate leads to the growth of an oxide with a more ordered structure (higher transmission, but also greater resistivity), and in order to make up for the number of defects in the film required for the formation of the best conductivity, it is necessary to increase the growth rate.

On the one hand, a decrease in the distance from the magnetron to the sample should lead to greater damage to the sample surface due to a weak attenuation of the kinetic energy of plasma particles at a small distance from the region of its generation. On the other hand, the growth rate of the oxide increases markedly with this arrangement and in a shorter period of time, the sample surface is completely covered with an ITO layer, which is a kind of protective mask from subsequent plasma exposure. Considering this circumstance, a further decrease in the magnetron power may lead to more severe damage to the sample surface due to the longer exposure time of the plasma to unprotected areas. Thus, it was shown that the rate of formation of ITO

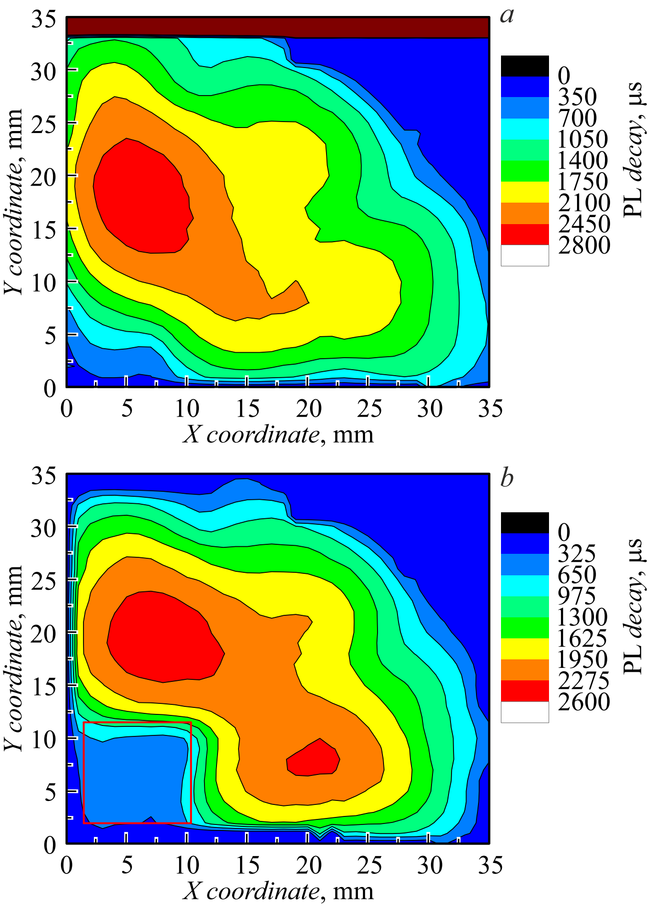

Figure 2. CCs lifetime distribution map for the sample a-Si : H/c-Si before (a) and after (b) ITO deposition at a distance from the magnetron to the substrate holder 7 cm.

films is an important parameter that significantly affects the degree of degradation of the heterointerface a-Si : H/c-Si.

Funding

The research presented in the paper was carried out as part of the state assignment of the Ministry of Science and Higher Education of the Russian Federation № 0791-2020-0004.

Conflict of interest

The authors declare that they have no conflict of interest.

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