Atmospheric adsorption effects in hot wire chemical vapour deposition microcrystalline silicon films with different electrode configurations

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Hot wire CVD thin silicon films were studied by means of dark conductivity, FTIR, hydrogen evolution and SEM surface characterization. Three types of metastability were observed: a) long term irreversible degradation due to oxidization processes on the film surface, b) reversible degradation determined by uncontrolled water/oxygen adsorption, c) fast field switching effect in the film bulk. We propose this effect is associated with morphology changes during film growth and electrical field induced by adsorbed atmospheric components on the film surface. It has been found that metastable processes close to the film surface are stronger than in the bulk.

1. Introduction

The hot wire chemical vapour deposition (HWCVD) technique [1–4] has been extensively studied in the deposition of silicon related materials at low temperatures without the use of plasma to decompose source gas. Metastability in microcrystalline thin silicon films deposited using high hydrogen dilution is probably one of the major issues limiting its applications for solar cells, thin-film transistors (TFT) and other devices. It is known that properties of thin silicon films are affected by atmospheric adsorption processes, aging. Both reversible (short term) and irreversible (long term) effects in conductivity on different kinds of thin film materials exposed to atmospheric air have been reported [5–9]. The irreversible effect was related to surface chemical reactions of oxygen incorporation processes [5] in amorphous silicon films. Reversible effects are related to physical adsorption of atmospheric components on the film surface. However, it is still unclear to what extent the material bulk is involved in aging process, or is this only a surface effect? In the present work we investigate the influence of exposure to atmospheric gases on both the bulk and surface of hot wire microcrystalline silicon films and we propose a model for the atmospheric components adsorption mechanism, based on obtained results. The results of the work can be used to improve the stability of hot wire microcrystalline silicon films to atmospheric processes.

2. Experimental

As an improvement to the conventional hot wire technique, a deposition system [1] incorporating independently controlled heated subsrate holders on both sides of the filaments has been built. The aim here was to increase effectiveness by depositing two different substrate temperature films in one process. Two straight tungsten filaments of 0.5 mm diameter and approximately 8 cm length each were placed between the substrate holders. The filament to substrate distance was kept constant at 5 cm. DC power was applied and the filament temperature was varied between 1500 and 2300°C. The hydrogen gas inlets to the reactor have been positioned to minimize silicide formation at the lower temperature regions at the clamped ends of the filaments. An optical pyrometer was used to monitor the filament temperature during the deposition process. Hydrogen diluted silane gas $(R = \{[SiH_4]/[SiH_4 + H_2]\} \cdot 100\% = 60\%)$ was introduced and the total gas pressure varied between 30 and 50 mTorr. In our experiments we have investigated silicon films with a thickness of about 1 μm.

To investigate atmosphere-induced metastable processes in detail, two types of coplanar contacts have been introduced: top aluminum contacts to control changes on the film surface and bottom chromium contacts to monitor bulk effects.

A series of microcrystalline silicon films have been deposited at substrate temperatures (varied between 200 and 500°C) for post deposition oxidization studies, using the HWCVD technique. The film growth proceeds by deposition of an amorphous phase and nucleation of crystallites followed by open structure growth. Fourier transform infrared (FTIR) spectroscopy has been used to investigate the content and bonding configuration of oxygen and hydrogen in the microcrystalline films (after deposition and 1.5 years later). The instrument used was a Mattson 7000 FTIR spectrometer. Scans were made in the 400–4000 cm^{-1} wavenumber range. Oxygen and hydrogen absorption peaks were integrated to calculate concentration values.

3. Results and discussions

Microcrystalline silicon films are known to show an increase in dark conductivity, associated with post deposition oxygen incorporation [7–9]. The films studied here show an irreversible (long term aging) increase in conductivity up to 2 orders of magnitude, over a period of 1.5 years. It

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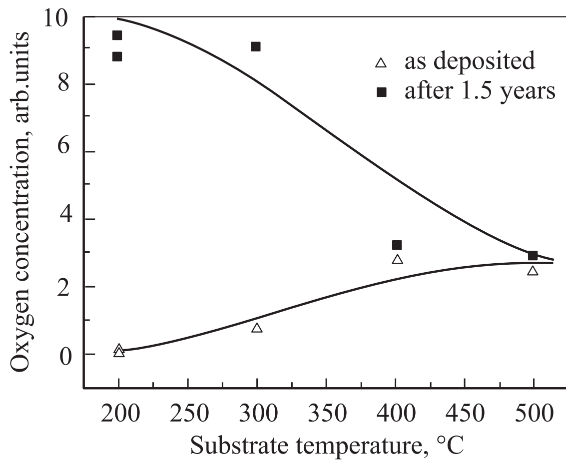

Figure 1. Post deposition oxidation effects in μc-Si films. $T_f = 1700°$C.

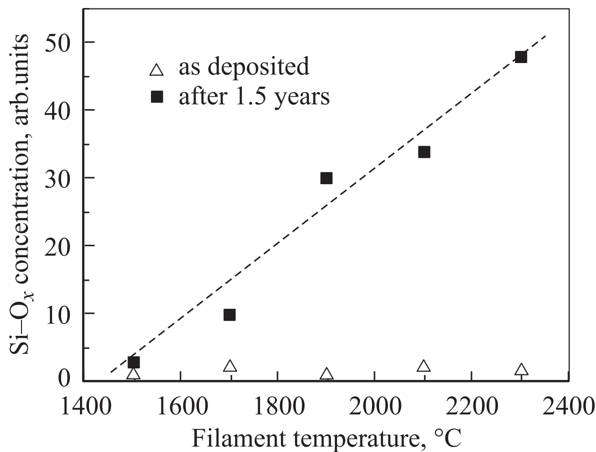

Figure 2. Post deposition oxidation effects in μc-Si films. $T_s = 300°$C.

was found that the largest conductivity increase corresponds to films deposited at low substrate temperature. To investigate a correlation between changes in conductivity and oxygen content, the FTIR measurements have been perfomed. Changes of oxygen concentration over a period of 1.5 years depending on a substrate temperature T_s at the constant filament temperature $T_f = 1700°$C are presented in Fig. 1. One can see that material deposited at temperatures higher than $T_s = 400°$C is almost not able to adsorb oxygen atoms with time. On the other hand, materials grown at low substrate temperatures are found to be more sensitive to the post deposition oxidization process. Hydrogen concentration measurements using FTIR technique were carried out on the films obtained with different substrate temperatures. The results (not presented here) show that hydrogen content decreases while substrate temperature rises. Both these facts suggest that compactness of the material increases with substrate temperature while material porosity decreases with temperature rise. Oxygen concentration changes over a period of 1.5 years depending on a filament temperature are presented in Fig. 2. The films were deposited at 300°C substrate temperature. It can be seen clearly that the silicon oxide concentration was initially very small but after 1.5 years is higher when the wire temperature is increased. At the wire temperature of 1500°C there is no increase in oxidation.

Note that conductivity values of as deposited films are in correlation with substrate temperature: the dark conductivity of the films deposited at $T_s = 400°$C is about 1 order of magnitude higher than of the films deposited at $T_s = 200°$C. It can be due to the higher oxygen concentration (see Fig. 2), when oxygen atoms act as donors and also due to crystallinity variations, when maximum crystallinity is obtained at $T_s = 400°$C [10]. This correlates with conductivity changes observed, confirming a dominant role of oxygen in the post deposition irrevesible increase of dark conductivity.

To clarify a contribution of both bulk and surface [11,12], reversible changes in dark conductivity were investigated

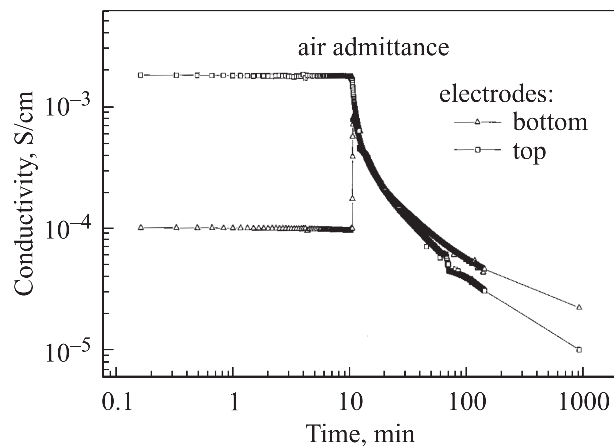

Figure 3. Effect of air admittance (admittance starts at 10th minute) on the dark conductivity in μc-Si films. Reversible by annealing.

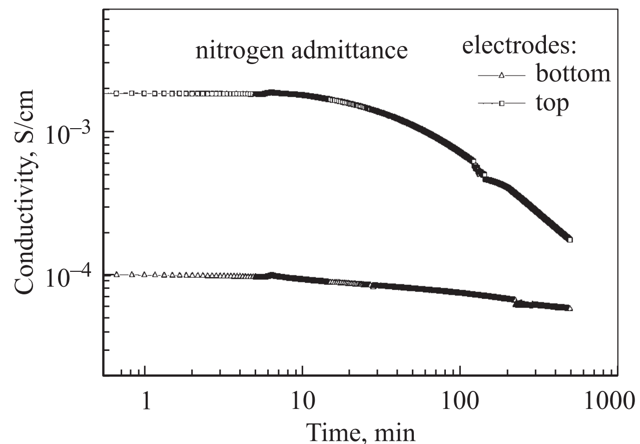

Figure 4. Effect of nitrogen on the dark conductivity in μc-Si films. Reversible by annealing.

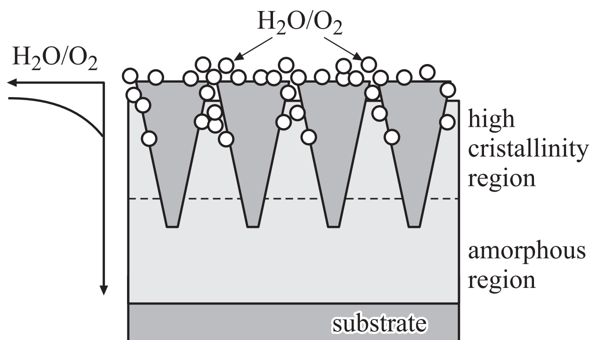

Figure 5. Atmospheric moisture adsorption in a microcrystalline silicon film.

on microcrystalline films with different electrode configurations. The films were deposited at substrate temperatures less than 300°C. The changes in film dark conductivity measured with coplanar electrodes on air admittance are presented in Fig. 3. The general trend shows dark conductivity decreases over many hours with exposure to atmosphere on the bottom and top electrodes. However, during the first few seconds conductivity on the bottom electrodes rapidly rises, giving a sharply pronounced peak. The fast conductivity change is associated with atmospheric gas adsorption [7]. The changes can be reversed by heating in vacuum at 180°C removing the adsorbed water. A response on air admittance, obtained on the bottom electrode, suggests that the material bulk is involved in atmospheric gas adsorption process. The rapid peak is associated with surface adsorbed atmospheric components; the proposed model of this effect is discussed below.

We also investigated an effect of selected gases on coplanar dark conductivity changes. Effect of nitrogen (Fig. 4) on dark conductivity has similar direction of changes as during water/oxygen adsorption. However, the sharp conductivity peak on the amorphous region (bottom electrodes) was not observed. The influence of nitrogen on surface conductivity is smaller than in the case of water adsorption (see Fig. 3). One of the possible explanations is that the penetrating nitrogen molecules are electro-neutral in comparison to water molecules; however, residual amount of atmospheric gases might participate in this process.

Our model of atmospheric gas adsorption in microcrystalline silicon was proposed to explain the difference in results obtained for bulk and surface of the material, correlated with the data of atomic-force microscopy (AFM) and FTIR measurements. The AFM studies [8] show a homogeneous distribution of grains over the film area. For the $1\,\mu$m film thickness, typical grain sizes were ~ 50 nm, grains are mainly joined into „cauliflower-like“ conglomerates. A slight increase in grain size was observed for higher substrate temperatures. The RMS surface roughness in the investigated structures was about 25–30 nm. Such morphology suggests a presence of high porosity structure that might be sensitive to atmospheric components incorporation. Oxidized „cauliflower-like“ highly developed microcrystalline silicon surface instantly attracts molecules of H_2O or O_2 (FTIR observations) after exposing it to atmospheric air. A schematic diagram of hot wire microcrystalline silicon film morphology and water moisture adsorption is presented in Fig. 5. It is known that the adsorption of atmospheric moisture can change conductivity in both directions [7–9] depending on material microstructure. Highly crystalline structures show a conductivity decrease, while more amorphous materials show an increase of conductivity. The different behavior observed on bottom and top electrodes is associated with morphological changes during material growth. On air admittance we observe a conductivity decrease on the top electrode, which is an expected behavior for a highly crystalline material. It is proposed that H_2O molecules are first chemisorbed at certain surface sites and adsorbed components collect electrons from the material. Adsorbed molecules accumulate a negative space charge layer on the μc-Si surface when it is oxidised, as for crystalline silicon described by Jäntsch [13]. On the other hand the bottom contact reflects conductivity changes of the more amorphous region, where the adsorbed components give electrons to the material, raising the conductivity. Differently charged adsorbates create an electric field, perpendicular to the substrate, which is associated with a different behavior observed on the top and the bottom electrodes. The field provides extra charge carriers for the amorphous region, shifting the Fermi level up to the conduction band and giving a rapid conductivity rise. Thus, water donates electrons to the amorphous region and collects electrons from the crystalline region, providing different behavior observed on the bottom and the top electrodes. Because the „working“ area of the highly crystalline material is much larger, the effect of conductivity decrease becomes dominant with time. A much slower reaction occurs, decreasing the field, when chemisorbed water reacts with a bridging oxygen Si–O–Si at the interface and forms two non-bridging silanol groups Si–O–H which are neutral. This slow reaction decreases an electron concentration in the amorphous region, and together with a contribution from crystalline part, give a slow conductivity decrease. Silanol is unstable and releases H_2O at temperatures above 100°C, which explains vacuum annealing removal of water-induced metastability. It provides a possibility of complete removal of adsorbed components. The reproducibility of short term aging cycles has been obtained during 10 experimental cycles, giving an error within 20%, mainly determined by air humidity variations.

4. Conclusions

Hot wire microcrystalline silicon films are sensitive to an atmospheric gas exposure. The material microstructure significantly depends on the substrate and the filament temperatures. More compact materials were obtained

at low filament temperatures (below 1700°C) and at high substrate temperatures (over 400°C). At substrate temperatures below 300°C microcrystalline films are likely to be porous. Such porous films are found to be strongly affected by an oxygen incorporation irreversible process. Reversible processes on the film surface involve water vapour/oxygen adsorption and field accumulated by moisture that induces the band bending and the Fermi level shift. Different responses observed on air admittance are associated with microstructure changes during the material growth. Adsorbed moisture can be removed from the material by annealing at temperatures around 180°C. Investigations of material properties according to thickness variations and corresponding conductivity changes weve performed. Our further work includes studies of chemical processes on the surface and in the bulk involving *X*-ray photo spectroscopy depth profiling.

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