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On the transformation of a-Si:H surface to very thin insulating overlayer of device quality due to very low-energy particle impacts

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Formation of device-quality very thin insulating layer (VTIL) is of utmost importance for semiconductor based technology as well as thin film physics. A physical description of the growth of such layers on a-Si:H by low-energy argon ion impacts has neither been clarified nor dealt with yet. We have investigated the transformation of intrinsic a-Si:H thin film surfaces under the influence of two different sources of low-energy particles, namely low-temperature plasmas and low-energy ion beams. Electrical properties were investigated by C-V and I-V measurements and by charge version of deep level transient spectroscopy (DLTS) technique. For the characterization of structural properties of the samples, X-ray diffraction at grazing incidence (XRDGI) was used. The results obtained have enabled us to make conclusions concerning the electrical and structural properties of the film surfaces and their response to the impacts, the disturbance of semiconductor thin film volume lying just below VTIL created and the utilization of such structures in commercial production of thin film transistors (TFT) and amorphous thin film solar cells.

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1. Introduction

Recently we have developed a new technique, including its technical realization, for the investigation of density of states in amorphous silicon based semiconductors [1]. The method is based on an original way to form a device-quality very thin insulating layer (VTIL) in the surface region of amorphous semiconductors utilizing low-energy ion beam [2] which was investigated on a new charge deep level transient equipment (Q-DLTS) enabling us also the measurements of solid state voltcoulometry on thin film a-Si:H structures [3]. A very thin dielectric overlayer is needed for the realization of different operations and measurements on semiconductor films under high voltages to prevent their damage.

It was shown that gap states g(E) in amorphous silicon could be investigated by DLTS technique. Lang et al [4] and Cohen et al [5] presented a relationship between the density of gap states and DLTS spectra. The form of DLTS spectra is very close to the shape of g(E). There is a lack of new experimental results obtained on amorphous hydrogenated silicon (a-Si:H) using DLTS technique or dealing with the gap states on the basis of electrical methods (see review papers in [6]). The results on a-SiGe:H alloy are very poor.

The defect-pool model of Wiener [7] and Powell and Deane [8, 9] was used for the interpretation of our results obtained by Q-DLTS. The model includes three basic groups of states, namely at 0.63 eV (D_h), 0.82 eV (D_z), and 1.25 eV (D_e) which were identified by our charge version of DLTS [1]. Our experiments indicate that the model of Powell and Dean is the most reliable one amongst others for a-Si:H semiconductor.

Semiconductor gap states are closely related to the structural properties, especially to the density of dangling bonds formed due to the interaction with energetic ions. As the most topical problem, the investigation of medium range order and formation of microcrystallities in a-Si:H semiconductor [10] can be mentioned.

In this paper, we focus our attention on the comparison of two techniques leading to the formation of device quality VTIL from the point of view of electrical and structural properties. Low energy ion beam treatment and low temperature rf plasma exposure were used to modify the semiconductor surface. We discuss the changes induced in the gap-state distribution and structural modifications caused by the interactions. Further, we present the way how to suppress the interface states in the plasma treated a-Si:H structures. Finally, an original type of I-V measurements to tailor a drift of hydrogen ions in the film is reported.

2. Sample preparation

Device-quality intrinsic a-Si:H layers of a thickness of ~ 1 μm were deposited on n-type Si(100) oriented crystals (phosphorus doped of 1-10 Ωcm resisitivity) in a 13.56 MHz rf excited parallel plate plasma enhanced chemical vapor deposition system from pure SiH_4 and its mixture with H_2 and GeH_4 at the plasma power of ~ 40 W, the sample temperature ranging from 190°C to 250°C.

In the surface region of both types of amorphous silicon based thin films, ultrathin insulating overlayers were formed by the following procedures:

i) Argon plasma treatment in a commercial rf plasma capacitively coupled equipment SECON XPL-200P was done. The frequency and power of the rf generator were 100 KHz and 60 W, respectively. The temperatures of the samples were kept in the 20 - 30°C range. A set of three samples was prepared at the working pressures of 200 μbar, 500 μbar and 900 μbar of high purity Ar. Special attention was paid to the first sample which has the best resistance. From the volt-ampere characteristics measured by a cylindrical probe located in the central part of the plasma at 500 μbar, the following values of the plasma potential, ion density, electron temperature and ion flow density were determined, respectively : 45 V, $5x10^{14}$ m^{-3}, 3.0 eV and $1x10^{17}$ m^{-2} s^{-1}.

ii) Ion beam exposure was done in two steps at the sample temperature of 80 °C. First, a treatment by 350 eV argon positively charged particles with the dose of ~ 10^{16} per cm^2 was applied followed by the covering of the exposed surface by an insulator using a low-energy ion beam, composed of oxygen and hydrogen only, with the dose of ~ $2x10^{15}$ per cm^2. This type of the samples served as a reference for those prepared by plasma treatment. Previous results obtained on similar structures were published e.g. in [1, 3, 6].

3. Experiment, results, and discussion

3.1 Charge version of deep level transient spectroscopy (Q-DLTS), capacitance-voltage (C-V) and current-voltage (I-V) dependences

The metal (gold)-oxide-amorphous semiconductor (MOS) structures were used for the modified charge-based correlation DLTS measurements [11]. This method is based on the use of a weighted combination of the charge-based DLTS measurements of the transient response of the MOS structure under periodically applied voltage steps to the gate electrode. The time events, when the signal is measured, as well as the weighting coefficients used are chosen with regard to the requirement to improve the selectivity in the decomposed spectrum. The resulting correlated charge DLTS signal, S_c, is described by a weighted summation of the contributions coming from three channels. In the presence of a leakage current, there is a parasitic output charge that is to be eliminated. At a selected temperature, T, this component represents a

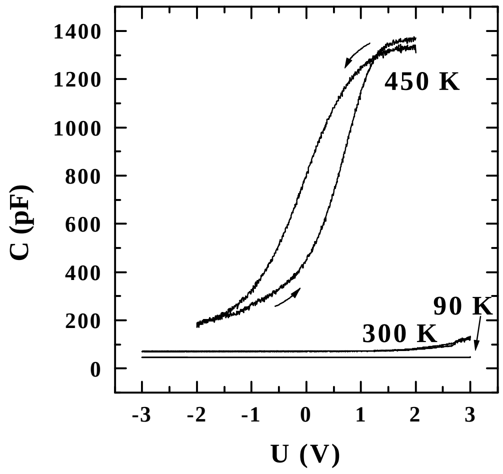

Figure 1. C-V curves of the sample prepared at 200 μbar by the oxygen plasma exposure.

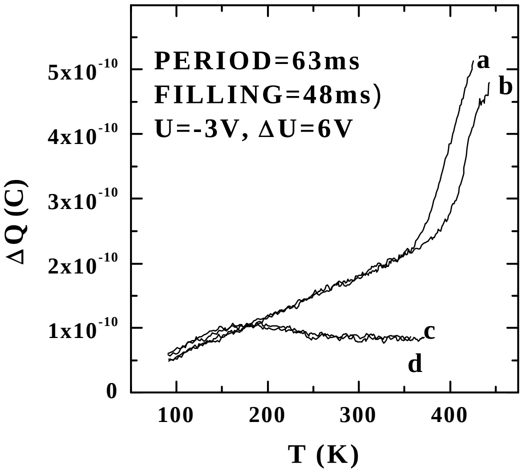

Figure 2. Q-DLTS measurement of the 200 μbar sample without annealing (a) and with thermal annealing at 490 K (i.e. at bias 0 V), 10 min (b), +4 V, 490 K, 10 min (c), -4 V, 490 K, 10 min (d). Thermal annealing at 490 K itself does not modify the Q-DLTS spectrum.

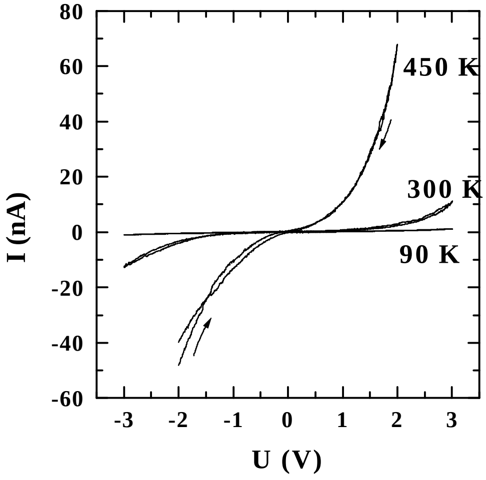

Figure 3. I-V dependence of the 200 μbar sample.

linear drift that is effectively suppressed by a correlation DLTS filter. The following formula for the evaluation of the DLTS signal was used :

$$\Delta Q \approx \left[\frac{C_{ox}}{C_{ox}+C_s}\right] q\cdot w\cdot N_T\cdot \exp(-e_n t) \qquad (1)$$

where w, N_T, C_{ox} and C_s are the excited part of the depletion region; the trap density, the capacitance of the oxide, and the capacitance of the space charge layer, respectively. The emission rate from the trap at the energy ΔE is

$$e_n = v\cdot s_n\cdot N_c\cdot \exp\left(-\frac{\Delta E}{kT}\right) \qquad (2)$$

where s_n is the capture cross section and the N_c is the effective density of states in the conduction band. The sampling times have been chosen to be t_1, $2t_1$ and $4t_1$. The resulting correlated charge DLTS signal, S_c, was determined as

$$S_c = Q(t_1) - 1.5Q(2t_1) + 0.5Q(4t_1) \qquad (3)$$

The C-V and I-V curves were measured using the rates of 0.02 Vs^{-1} and 0.1 Vs^{-1}, respectively. Al gates of an area of 0.34 mm^2 were fabricated by evaporation in a vacuum equipment. The fabricated Schottky diodes were not subjected to any annealing procedure. For getting basic C-V characteristics of the diodes, the feedback charge capacitance technique was applied. The experimental results obtained by C-V, Q-DLTS and I-V methods on the samples prepared by the oxygen plasma exposure at the pressure of 200 μbar are shown in Figs.1-3, respectively.Electrical properties of the structure prepared at the pressure of 500 μbar are illustrated in Figs. 4-6. The properties of 900 μbar sample were not possible to evaluate due to a large leakage current.

The samples prepared by argon ion beams contain three basic groups of states, namely at 0.63 eV (D_h), 0.82 eV (D_z), and 1.25 eV (D_e, as it was published in [12]. We can state that :

i) High resistive VTILs with the capacitance of ~ 1400 pF were prepared (Fig.1 and Fig. 4). The result is similar to the experiments with a low energy argon ion beam exposure and plasma ion implantation [12].

ii) The deep level spectra contain only the high temperature tail which can be suppressed by a bias annealing procedure (see Fig.2). We suppose that the tail observed is a rest of D_z states. It is not the signal caused only by an increased electrical conductivity of the system.

iii) I-V measurements did not confirm a motion of hydrogen. In the positive case, the volt-ampere wave peak at negative voltages (between -0.6 V and -0.7 V) should be observed [13]. The results of the corresponding measurement are shown in Fig.3 and Fig. 6.

The electrical measurements are in agreement with the optical ones (unpublished) as they confirm that a-Si:H layers lost their typical character given by the hydrogen

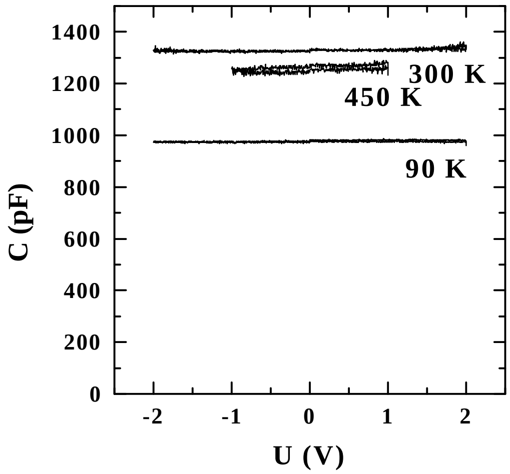

Figure 4. C-V curves of the sample prepared at 500 μbar by the oxygen plasma exposure.

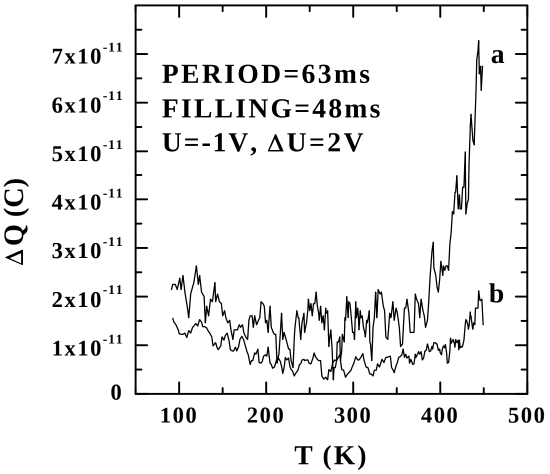

Figure 5. Q-DLTS measurement of the 500 μbar sample without annealing (a) and with thermal annealing at 490 K (i.e. at bias 0 V), 10 min (b).

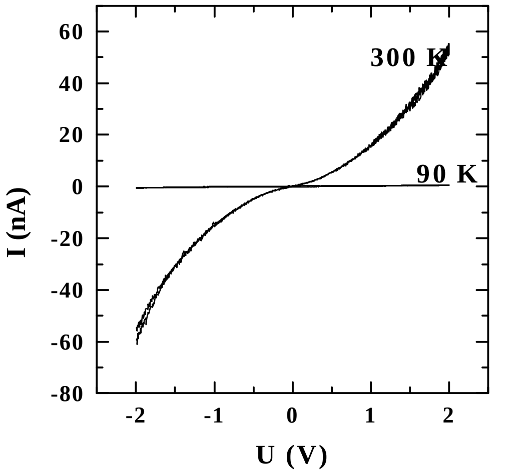

Figure 6. I-V dependence of the 500 μbar sample.

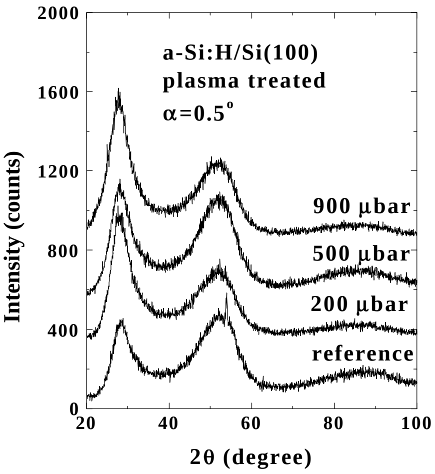

Figure 7. XRDGI patterns of the plasma exposed samples taken at the incidence angle of 0.5°.

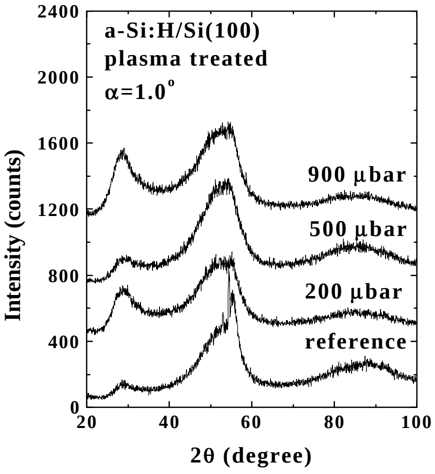

Figure 8. XRDGI patterns of the plasma exposed samples taken at the incidence angle of 1°.

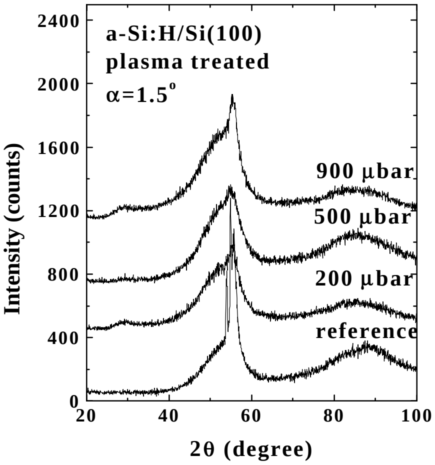

Figure 9. XRDGI patterns of the plasma exposed samples taken at the incidence angle of 1.5°.

content. We suppose that the hydrogen content in the layers was considerably decreased. After the interaction, a polycrystalline Si state characterized by both reduced density of hydrogen related bonds and some oxygen content begins to dominate. If a higher density of hydrogen remained in the samples after the interaction, the groups of states D_h, D_z, D_e could be observed. In the case that hydrogen was removed from amorphous layer, we would have measured only a constant DLTS signal corresponding to a low continuous density of states coming from the interface between the VTIL and amorphous and/or polycrystalline unhydrogenated silicon.

3.2 X-ray diffraction at grazing incidence (XRDGI)

The XRDGI was measured on a 12 kW Rigaku rotating-anode generator with the CuK_α radiation using a wide-angle position sensitive Inel detector. The diffractometer was equipped with a graphite monochromator in the primary beam. The grazing incidence angles were set to $\alpha = 0.5°$, 1.0° and 1.5°. The samples with the crystalline silicon (100) substrate were measured. Figs. 7-9 illustrate the typical shape of the XRDGI patterns taken on the reference ~ 1 μm thick a-Si:H/Si(100) structure. The dominant signal comes from the amorphized (100) cubic surface, namely 311 and 422 diffractions. An additional signal observed at ~ 28° is typical for the a-Si:H layer. Its intensity decreases with increasing incidence angle, i.e. with the increasing depth the diffracted X-rays come from. This maximum could be identified (using the PDF 2 database [14]) as the diffraction originating from the multiatomic Si-H groups such as $Si_{80}H_{20}$ complexes.

The XRDGI patterns taken from the whole pressure set of the samples prepared by plasma treatment at 0.5°, 1.0° and 1.5° incidence angles are shown in Figs.7-9. We can state that all plasma exposed samples have an increased density of $Si_{80}H_{20}$ complexes (see the development of the angular region around $2\Theta = 28°$). This result is in accord with the results of both optical and electrical measurements and confirms a drastic decrease of the hydrogen content in the a-Si:H thin films after the oxygen plasma treatment.

The XRDGI patterns taken from the samples exposed to low energy argon ion beam are shown in [2].

Comparing XRDGI patterns of both types of the samples (plasma vs. ion beam treated), a difference in the evolution of the diffraction maximum at 28.5° is dominant. Plasma exposed samples contain a higher content of $Si_{80}H_{20}$ complexes after irradiation while the ion beam treated a-Si:H thin films have a lower density of the complexes in comparison with the reference sample. We interpret this different behaviour as a consequence of the one-order difference in the applied fluences of the particles impinging on the surface, namely $\sim 10^{17}$ cm^{-2} and $\sim 10^{16}$ cm^{-2} for plasma and ion beam exposure, respectively. We relate this effect mainly to the increase of the temperature of the a-Si:H due to the higher fluence applied. The influence of the higher temperature prevails over the destruction of multiatomic complexes by particle impacts. Therefore, the plasma exposure leads to the formation of VTIL/a-Si:H structure with an increased density of ordered polycrystalline-like hydrogenated silicon complexes.

4. Conclusions

It was shown that the electrical and structural properties of virgin a-Si:H thin film of 1 μm thickness deposited on c-Si(100) were considerably transformed after the interaction with both low temperature rf oxygen plasma of short duration and low energy ion beams. The following conclusions may be done :

i) High resistive VTILs of device quality of 7-10 nm thickness were prepared in both cases (plasma and ion beam treatment) in the surface region of a-Si:H. For the plasma experiments, the most suitable pressure of oxygen is 200 μbar. The result is similar to the experiments with a low energy argon ion beam.

ii) The deep level spectra of the plasma treated samples contain only a high temperature tail which can be fully suppressed by a bias annealing procedure. It means that we prepared the sample without any deep states at the measured interface. We suppose that the observed tail is a rest of D_z states. The Ar ion beam treated samples contain three regular groups of states, namely D_h, D_z, D_e.

iii) A drift of hydrogen in the structures was not observed by voltcoulometric measurements.

iv) All plasma exposed samples demonstrate that an increased part of the volume is occupied by $Si_{80}H_{20}$ complexes as judged from an increased intensity of the corresponding diffraction peak.

v) Contrarily, a decrease of the complex concentration is typical for the ion beam treated samples.

vi) All types of measurements confirmed a considerable decrease of the hydrogen content in the a-Si:H thin films after the oxygen plasma treatment and the formation of a-Si:H:O semiconductor inhomogeneous layer.

We interpret the different behaviour of the plasma and ion beam treated samples as a consequence of the one-order difference in the applied fluences of the particles impinging on the surface during the experiment, namely $\sim 10^{17}$ cm^{-2} and $\sim 10^{16}$ cm^{-2} for plasma and ion beam exposure, respectively. We suppose that a recrystallization of the amorphous surface region is observed at higher fluences (plasma treatment).

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