On metastable properties of plasma treated amorphous Si:H films

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Amorphous hydrogenated silicon (a-Si:H) is well known as a semiconductor with metastable properties. This paper deals with structural and electrical properties of a-Si:H surfaces in virgin state as well as on low-energy ion exposition. Two ion sources were used, namely a monoenergetic ion beam produced by Kaufmann source and ions extracted by the plasma immersion ion implantation technique (PIII). The structural and electronic changes induced by ion impacts, as investigated by the X-ray diffraction at grazing incidence, capacitance-voltage measurements and charge version of deep level transient spectroscopy (Q-DLTS) are reported. The changes induced in the gap-state distribution of a-Si:H due to an interaction with low energy Ar^+ ions followed *in situ* by the short exposure to both hydrogen/oxygen ion beam or to molecular high-purity oxygen are presented. The X-ray measurements confirmed that the most important reflection, which enables us to trace the evolution of the structural changes of a-Si:H layers caused by ion impacts, has the position at $2q$ ~ 28°. It is related to the existence of $Si_{80}H_{20}$ complexes inside the layer. The existence of only two types of deep metastable distributions D_z and D_e was observed in MIS structures prepared for the first time by the plasma immersion ion implantation technique. The distribution corresponding to positively charged defects D_h is missing. The use of the standard monoenergetic ion beam technique for the preparation of MIS structure confirmed the existence of three types of deep metastable distributions in a-Si:H (D_h, D_z and D_e). The differences in the results are explained by the application of a relatively high negative potential (1000 V) on the sample during the PIII experiments.

Keywords: Metastability; Amorphous semiconductors; Structural properties; DLTS; Plasma immersion ion implantation; Very thin oxide

1. Introduction

The formation of an electrically stable very thin insulating layer (VTIL) has been of utmost importance in the field of LSI technology (e.g. surface passivation, diffusion masking and insulating layer preparation). The most significant application of SiO_2 VTIL in LSI technology is the gate oxide in DRAM and tunnel-oxide in flash memories. With the increase of integration scale, the device dimensions are decreasing rapidly. Hence, the quality of SiO_2 VTIL needs to be considerably improved. Small amounts of defects in SiO_2 VTIL affect strongly the stability and reliability of metal-oxide-semiconductor (MOS) devices. One of the most critical problems is the dielectric breakdown of MOS device which is probably initiated by charge trapping coming from the defects localized in the volume of SiO_2 VTIL.

Recently, we have developed a technology for the preparation of high quality very thin SiO_2 layers with the assistance of very-low-energy particle beams in the surface region of the amorphous silicon-based semiconductors including e.g. such a silicon alloy as a-SiGe:H [1-3]. VTILs prepared in this way are grown into the amorphous semiconductor surface and therefore they are formed by the transformation of the uppermost semiconductor surface layers by the impacts of monoenergetic atoms (Ar, H and O - or their mixture).

The intrinsic a-Si:H represents a dominant part of amorphous silicon solar cells. The performance of amorphous silicon solar cells is dependent also on the spatial defect distribution in the intrinsic layer of the device, in particular the dangling bonds [4, 5]. Depending on the energies of the quasi-Fermi levels in the band gap, these dangling bonds act as deep traps or recombination

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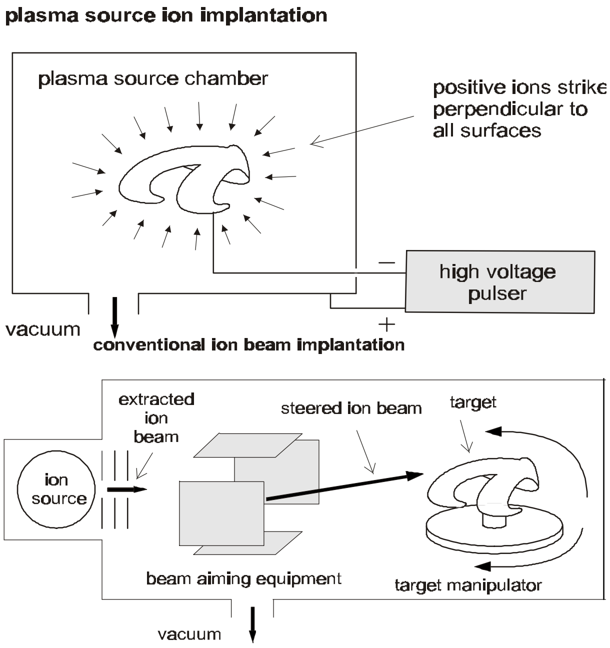


Figure 1. Scheme of the plasma immersion ion implantation (PIII) and the conventional ion beam implantation techniques.

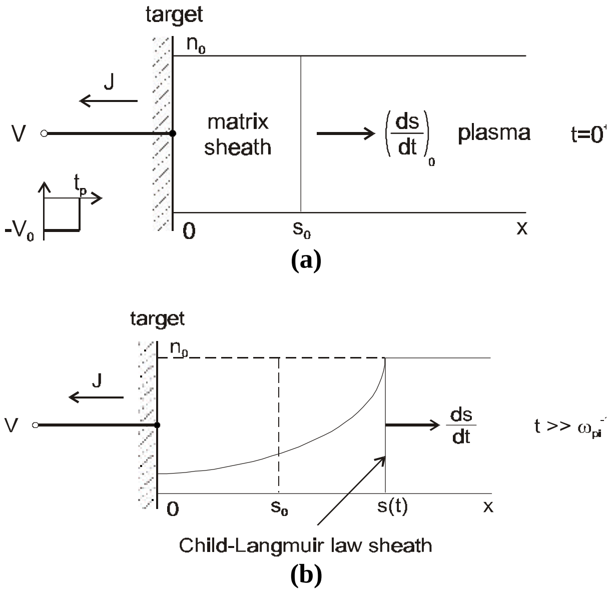


Figure 2. hnique immediately after the applied negative pulse (a) and after the time ~ w_{pi}^{-1} (b).

levels and hence affect the properties of a device. According to the defect-pool model [6], the energy distribution of the gap states (EDOS) is determined by the width of the valence band tail and by the energy of the equilibrium Fermi level in the band gap. The position of the Fermi level in the band gap is responsible for the shape of EDOS in the gap [6]. According to the prediction of the defect-pool model, the peak of the EDOS is in the lower (upper) part of the band gap if the Fermi level is near to the conduction (valence) band.

In this paper, we present metastable electronic properties induced in the gap-state distribution of a-Si:H due to an interaction with low-energy Ar^+ ions followed by an *in situ* short exposure to either hydrogen/oxygen ion beam or to a molecular high-purity oxygen beam. Low-energy particles came from :

i) monoenergetic ion sources (up to 500 eV) - an interaction with low-energy Ar^+ ions followed *in situ* by a short exposure to both hydrogen/oxygen ion beam or to molecular high-purity oxygen and

ii) RF plasma source by using the plasma immersion ion implantation technique which provides accelerated oxygen ions of 1000 eV kinetic energy.

2. Experiment

Electrical, optical and structural parameters of the exposed surfaces were investigated to study the complex character of the surface transformation initiated by low-energy particle impacts. Device-quality intrinsic a-Si:H layers with the thickness of 0.9 μm were deposited on crystalline silicon substrates in 13.56 MHz RF excited parallel plate plasma-enhanced chemical vapour deposition system from pure SiH_4 gas at plasma power of 35 W and the temperature of 250 °C.

The exposures of the samples were performed in :

i) ion beam etching system of LPAI Comp. The ion beam exposure was usually done in two steps:

A) the treatment by 350 eV positively charged Ar^+ particles with a dose of ~ 10^{16}/cm^2;

B) the covering of the exposed surface by a very thin insulating layer prepared by low-energy ion beam composed of oxygen and hydrogen only, the dose being ~$2x10^{15}$ /cm^2.

ii) laboratory plasma system constructed for the plasma immersion ion implantation (PIII) using oxygen plasma. A high-doped n-type c-silicon wafer with (100) surface orientation was used as substrate. Samples with an area of 1.0 cm x 0.5 cm were O_2 implanted. The working pressure in the system was 5.10^{-2} Pa, the amplitude of negative voltage pulses was ~ -1 kV and the frequency was 100 Hz. The samples were implanted for 1 hour which, according to the Lieberman's PIII model, produces roughly equal an implantation dose of 3.10^{15} cm^{-2}.

The latter exposure system has never been used for the formation of thin dielectric overlayers in the a-Si:H technology. This method is used for surface modifications of metals, crystalline semiconductors and dielectrics. A modification is represented by the implantation of gas atoms (gas ions) into the material that change structure and composition of the near-surface region of the target. In this way, it is possible to create a new layer with different properties which is not deposited onto the substrate but grown into it. Strong adhesion of such a kind of thin film is achieved. Good homogeneity, structure and morphology can be achieved as well.

The main differences between PIII and conventional ion beam implantation (IBI) are visible from Fig. 1. A compact implantation equipment is used for PIII. The plasma created in the chamber surrounds the target. The ions are extracted from the plasma and accelerated by a negative voltage pulse applied to the target. In conventional ion beam implantation, the process is divided into several steps. The ions are created in the ion source and consequently an ion beam is created and steered by a special equipment. The target is usually a flat plate. In the case of 3D target, its manipulation is inevitable to satisfy homogeneous implantation.

The ion source in PIII is plasma. During the implantation process, the target is inserted into the system. The plasma surrounds the target. A negative voltage pulse is then applied to the sample. In a time scale of $t \sim w_{pe}^{-1}$ (inverse electron plasma frequency), the electrons are repelled from the sample (they have a higher mobility because of their lower mass) and an ion matrix sheath is created (Fig. 2a). In a time scale of $t \sim w_{pi}^{-1}$ (inverse ion plasma frequency), the ions are accelerated towards the sample. To get the maximum energy from the electric field, a collisionless sheath is needed. This condition is usually satisfied by a low pressure in the system. During the implantation, the sheath is extending according to the Child-Langmuir law (Fig. 2b) until a steady-state is achieved. The number of the implanted ions, called implantation dose, is given by $N = n_0.s_T$, where n_0 is the concentration of the positively charged ions and s_T is the steady-state thickness of the sheath. To provide a required implantation dose, new positively charged ions have to be created beside the target. After switching off the applied negative pulse, the plasma will extend back to the sample. The new ions can be implanted by applying the negative pulse again. The whole process is repeated until a required implantation dose is achieved.

The following experimental methods were used for sample characterization:

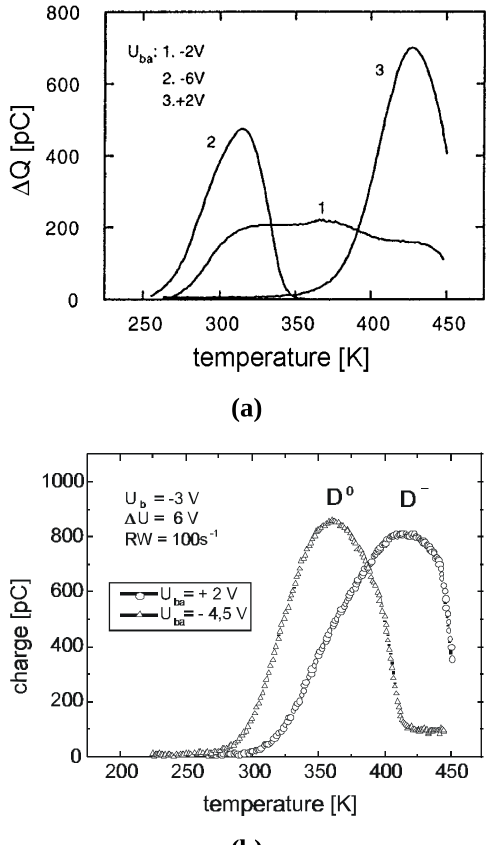
i/ X-ray diffraction at grazing incidence (XRDGI) that was measured on the 12 kW rotating anode RIGAKU generator with the CuKα radiation

ii) charge version of the deep level transient spectroscopy (Q DLTS)

iii) capacitance-voltage measurements.

3. Experimental results and discussion

The XRDGI pattern from the ~ 1μm thick a-Si:H/(100) Si structure confirmed that the dominant reflections come from the amorphized 100 cubic surface, namely 311 and 422 ones. An additional reflection at $2q \sim 28°$ is typical for the a-Si:H layer. Its intensity usually decreases with the increasing angle of incidence. This reflection could be identified using the PDF database [7] as the reflection originating from multiatomic Si-H groups ($Si_{80}H_{20}$ complex) whose number is determined also by the impact process and its parameters (type of ions, energy, fluence etc.).



(a)

(b)

Figure 3. The Q-DLTS spectra of the undoped a-Si:H (a) annealed at the equilibrium temperature of 500 K for 10 min. and with different U_{ba}. The spectra were measured with the bias voltage U_b = -3 V, the filling pulses up to 0 V and the rate window of 50 s^{-1}. The energies of the defect states at the peak maxima 2 and 3 are 0.63 eV and 1.25 eV, respectively. The samples were prepared by monoenergetic ion beams, (b) annealed at the equilibrium temperature of 500 K for 10 min. and different U_{ba}. The spectra were measured with the bias voltage U_b = -3 V, the filling pulses up to + 3 V and the rate window of 100 s^{-1}. The samples were prepared by the PIII technique.

In the amorphous silicon based films, an EDOS can be "predefined" by annealing at 500 K, which is just above the equilibrium one, for 10 minutes at a particular bias voltage, U_{ba} (so-called bias annealing procedure). Three distinct distributions can be usually prepared consisting of the D_h, D_z and D_e dangling metastable bond components:

∗ intrinsic distribution (U_{ba} = -2V); usually all three components are present (D_h, D_z and D_e);

∗ n-type distribution (U_{ba} = +2V); mainly the D_e component is present;

∗ p-type distribution (U_{ba} = -6V); mainly the D_h component is present.

The peak positions of the D_h, D_z and D_e components correspond to the temperatures (activation energies measured from E_c) in the Q-DLTS spectra of 320 K (0.63 eV), 390 K (0.82 eV) and 430 K (1.25 eV), respectively (see Fig.3a).

The samples treated by the low-energy ion beam and plasma immersion ion implantation (PIII) techniques were inspected by the Q-DLTS and C-V measurements. The results are illustrated in Fig.3b. The PIII experiments with a chosen energy of the impacting oxygen positive ions below 1000 eV and the doses of 10^{15} ions per cm^2 have resulted in the formation of the structures with the accummulation capacity of ~ 1200 - 1500 pF corresponding to the oxide thickness of 6 - 8 nm. The typical feature of the PIII samples is the missing group of 0.62 eV (D_h) states. The bias annealing at U_{ba} = + 2V at 500 K has created n-type distribution. The bias annealing at U_{ba} = **-** 4.5 V should lead to the distribution of p-type, however, the distribution with D_z dominant states was obtained only. Due to a lower electrical resistivity of the VTIL, it was not possible to anneal the samples at U_{ba} = **-** 6 V. Therefore only two groups of the metastable defects, namely 0.82 eV (D_z) and 1.25 eV (D_e), were found in the structures prepared by the PIII technology. We suppose that the PIII technology, using the implantation at the sample voltage of ~ **-** 1000 V, causes the formation of a-Si:H layers with the missing group of D_h states and that the decisive parameter determining the formation of only two groups of states is the negative potential of the sample during the implantation.

4. Conclusions

To eliminate the loss of measured signal, it is suitale to use the charge version of DLTS technique in which the transient current is integrated yielding thereby a charge transient. The integration renders the charge detection sensitivity independent of the time constant. The leakage current, which can affect the measured spectrum considerably, was reduced in our case by the presence of the insulating layer. In this way, the interface between the insulating layer and a-Si:H with a suppressed density of states was achieved, too, as the most damaged outer part of the semiconductor surface was partly sputtered off and/or transformed to dielectric. Unlike thermally grown or deposited insulating layers, the treatments used do not induce a high density of interface states. In fact, a MIS-like structure was obtained where quai-Fermi levels are not considered and the surface Fermi level can easily be shifted by the applied bias over the whole band gap. Therefore we can conclude that oxide layers of 5 **-** 10 nm thickness with a considerably suppressed interface density of states were prepared by both the monoenergetic ion beams and the plasma immersion ion implantation, the latter technique being used for this purpose for the first time.

Three basic groups of defect states in the band gap of a-Si:H were revealed and investigated. The gap states, *g(E)*, can be inspected by the charge version of deep level transient spectroscopy. A relationship between the density of the gap states and the form of Q DLTS spectra was found. At present, there is still a lack of new experimental results obtained on hydrogenated amorphous silicon using the DLTS technique. In agreement with the improved defect-pool model of Powell and Deane [6], we have been able to identify three basic metastable groups of states, namely 0.63 eV (D_h), 0.82 eV (D_z) and 1.25 eV (D_e), by charge version of DLTS (see Fig. 3). The ion beam etching LPAI system has been used for the preparation of the samples. The plasma immersion ion implantation leads to the formation of the samples in which only two groups of the metastable gap states were found, namely 0.82 eV (D_z) and 1.25 eV (D_e) (see Fig. 3). The existence of the group of states related to holes D_h was not confirmed in the structures prepared by the PIII method. We suppose that the plasma implantation with the bias voltage ~ **-**1000 V has similar consequences as continuous bias annealing of the sample during the deposition process and in comparison with the formation of dielectric layer by low energy ion beams it leads to a slightly lower interface state density. It may be supposed that the abundant negative charge eliminates D_h states (vanishing D_h peak). The effect of different values and polarities of the bias voltage needs to be inspected in the future.

The X-ray measurements revealed the presence of the reflection at the position $2q$ ~ 28° related to the existence of $Si_{80}H_{20}$ complexes inside the a-Si:H layer which enabled us to trace the evolution of structural changes caused by ion impacts.

Acknowledgements

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