CHARACTERIZATION OF HYDROGENATED SILICON THIN FILMS AND DIODE STRUCTURES WITH INTEGRATED SILICON AND GERMANIUM NANOPARTICLES

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Abstract

P-I-N diode structures based on the thin films of amorphous hydrogenated silicon (a-Si:H) deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD) technique were prepared with embedded Si and Ge nanoparticles. The Reactive Laser Ablation (RLA) of germanium target was used to cover the intrinsic a-Si:H layer by Ge NPs under a low pressure of the silane. The RLA was performed using focused excimer ArF laser beam under SiH_4 background atmosphere. Reaction between ablated Ge NPs and SiH_4 led to formation of Ge NPs covered by thin GeSi:H layer. The deposited NPs were covered and stabilized by a-Si:H layer by PECVD. Those two deposition processes were alternated repeatedly. Volt-ampere characteristics of final diode structures were measured in dark and under illumination as well as their electroluminescence spectra.

Keywords: a-Si:H, PIN diode, thin films, reactive laser ablation, nanoparticles

1. INTRODUCTION

Thin film semiconductor structures based of hydrogenated amorphous silicon (a-Si:H) prepared by plasma enhanced chemical vapor deposition (PECVD) are widely used for low cost and large area fabrication of optoelectronic devices, such as solar cells, light emitting diodes, sensors, etc. [1]. The nanocrystals and quantum dots are nanometer-scale semiconductor structures that represent one of the most intensively developing areas of modern semiconductor physics [2,3]. The semiconducting properties of Ge nanoparticles, especially convenient band gap, are reasons for the increase of absorption coefficient in the photon energy starting from 0.7 eV. Various forms of Si and Ge NPs are studied for other optoelectronic uses. It was shown that improved optical properties of Si and Ge NPs smaller than 5 nm are due to a combination of two effects: the stimulation of electron and hole radiative recombination rate due to increased overlap of electron and hole wave functions confined in the quantum dots (QDs) as well as the reduction of recombination rate via non-radiative defects.

In the last few years, we successfully applied the technological processes of the PECVD and molecular beam epitaxy for the deposition of the Ge NPs on the a-Si:H thin films [4-6]. We found the optimum deposition temperature to form nanocrystalline Ge particles on the surface of a-Si:H thin film to be 350°C. The Ge NPs were conglomerates of nanocrystals of size 10-15 nm and QDs with size below 2 nm embedded in amorphous Ge phase.

We have studied solar cells, which were p-i-n structures based on a-Si:H with nc-Ge inclusions in the i-type layer [7]. The characteristics of these structures were compared with those of similar structures but without nc-Ge. The results showed that the presence of Ge in the active region does not improve the solar cell characteristics; probably due to the fact that nc-Ge introduces additional recombination centers. On the other hand, we have shown that the photoluminescence intensity strongly correlates with the presence of isolated silicon nanoparticles in the mixed amorphous phase with embedded isolated silicon nanoparticles [8]. Thus, we have shown that the presence of Si NPs and related recombination centers can be used in light-emitting diodes and photodetectors for the visible and near-infrared ranges.

In this paper, we compare the volt-ampere characteristics and electroluminescence spectra of diodes based on thin film a-Si:H with and without embedded Si and Ge NPs. Our interest in this work is focused specially on the reactive laser ablation (RLA) technique which allows the formation of Ge nanocrystals with GeSi coat and their deposition on a-Si:H surface immediately after the interruption of the PECVD process. The combination of the RLA with PECVD is necessary requirement for the preparation of a-Si:H thin films with *in situ* integrated NPs.

2. EXPERIMENTAL

2.1. Plasma Enhanced Chemical Vapor Deposition and Reactive Laser Ablation

The thin film P-I-N diode structures were deposited from silane SiH_4 diluted in H_2 using the capacity coupled 13.56 MHz radio frequency glow discharge PECVD deposition process in stainless steal chamber with standard two electrodes configuration. The intrinsic layer was enriched *in-situ* with the presence of isolated silicon nanoparticles in the mixed amorphous and crystalline phase [8].

The intrinsic a-Si:H layers were also deposited by RF discharge technique (13.56 MHz, 20W) in the special glass chamber optimized for RLA, see the **Figure 1**. The pressure of silane was kept at 12 Pa by needle valve (1), the layers were deposited on substrate (2) placed on a heated and grounded holder. Germanium nanoparticles were then deposited by ArF laser ablation (100 mJ/pulse) from elemental Ge target (3). Pressure of silane was maintained at 0.5 Pa to cover NP by GeSi:H layer.

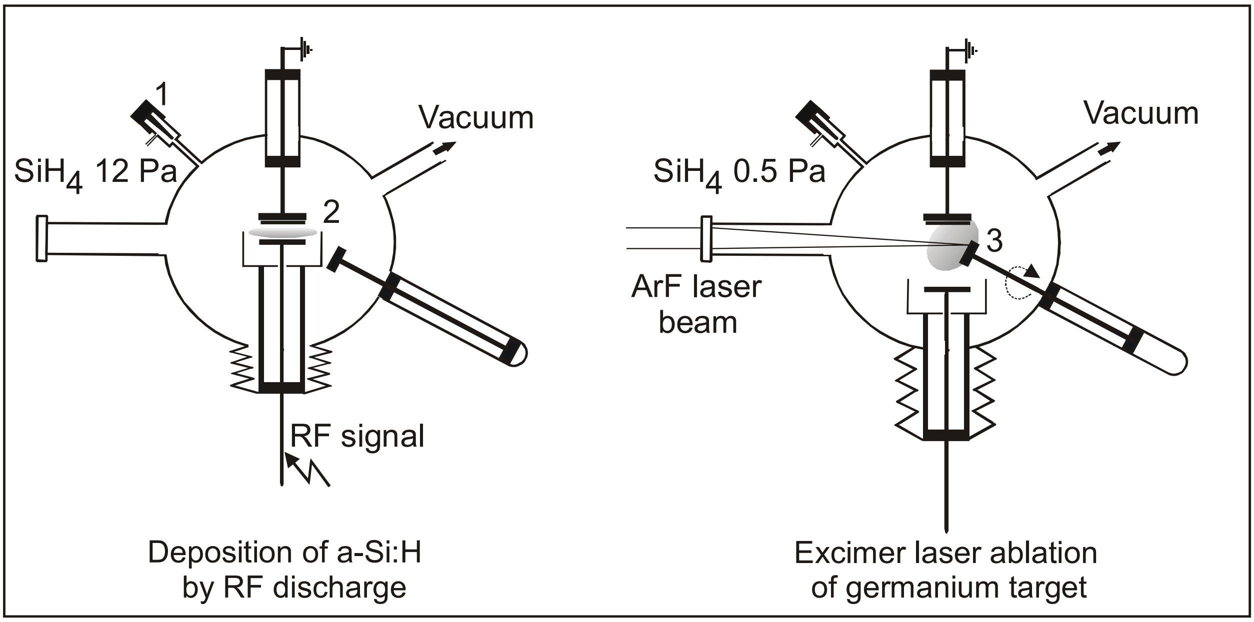

Figure 1 The schematic drawings of special glass vacuum chamber for the deposition a-Si:H thin films with embedded Ge NPs. The left picture shows the position of electrodes for RF PECVD deposition of a-Si:H. The right picture shows the position of target for his ablation by excimer laser.

We realized both deposition processes *in situ* and alternate them for the deposition of the intrinsic a-Si:H layer with embedded nanoparticles. However, the present configuration does not allow to deposit doped a-Si:H layers in the glass chamber used for laser ablation and thus to produce the complete N-type, intrinsic and P-type (P-I-N) diode structure *in-situ* in one deposition chamber. The P-type and the first intrinsic layer had to be made in the stainless CVD chamber, the second intrinsic layer with embedded nanoparticles in the glass chamber and the third intrinsic layer and N-type layer again in the stainless chamber. Therefore, the transfer between two deposition systems was necessary.

2.2. Volt-ampere characteristics

The volt-ampere characteristics were measured in the triggered pulse mode in dark and under light illumination. The Keithley Model 3390 Arbitrary Waveform/Function Generator was synchronized via TTL trigger line with Keithley Model 6485 Picoammeter (5 ½ digit resolution) and Thorlabs Model MWWHLP1 Mounted White LED. The LED provides the broad band illumination in 450-750 nm spectral range with maximum light output at the wavelength 600 nm and tunable light output power up to 2 W. Though, the applied LED illumination was not the solar simulator due to missing infrared light, the total light power density 100 mW/cm^2 had been calibrated with the certified a-Si:H thin film solar cell. The Keithley Model 3390 provides square voltage pulses with the amplitude up to ± 10 V (zero voltage is no available in pulsed mode, minimum amplitude is ± 20 mV. The voltage pulse duration is 25 ms at frequency 20 Hz. The current was measured using trigger delay 3 ms, the integration time 20 ms.

2.3. Electroluminescence spectroscopy

The steady-state electroluminescence spectra were measured at room temperature in the visible and near infrared spectra range 400 - 1600 nm in pulsed mode applying square voltage 50% duty cycle pulses at 10 Hz provided by the Keithley Model 3390 Arbitrary Waveform/Function Generator. The voltage amplitude was chosen to supply the forward current 3 mA. The electroluminescence light was collected by the f/1 objective to the monochromator HORIBA H20IR with spectral resolution 16 nm equipped with the Si and InGaAs photodiodes. The photodiode signal was detected by Signal Recovery Lock-in Amplifier Model 5105 referenced to TTL pulses synchronized with Keithley Model 3390 Arbitrary Waveform/Function Generator. The electroluminescence spectra were recalculated for the spectral efficiency of monochromator grating and detectors.

3. RESULTS AND DISCUSSION

The common problem when measuring volt-ampere characteristics in DC mode is heating the sample due resistivity losses related to the electric current and optical absorption of the incident light followed by the drift of the volt-ampere characteristics and the degradation of the material. Therefore, we applied two ways how to reduce these effects. First, the 50% duty cycle triggered pulsed mode has been implemented instead of DC mode and second, the time of measurement has been minimized by optimizing the voltage pulse frequency, voltage range and voltage step. It has been found that for our samples the voltage range from -1 to 2V with step 50 mV is sufficient. The voltage as well as light were on for 25 ms during each step. The current noise was significantly reduced by using trigger delay 3 ms when reading the current and by switching off the voltage source when changing the picoammeter range.

Figure 2 shows that the *ex-situ* deposition of the intrinsic a-Si:H layer without Ge NPs (#2) and with Ge NPs (#3) deteriorates forward current in comparison with the reference diode (#1), in which the deposition of the intrinsic layer was only interrupted. The complete P-I-N structure of the reference sample #1 including embedded Si nanoparticles has been prepared in the stainless steel PECVD chamber. The comparison shows the influence of the non-optimized intrinsic a-Si:H layer deposited in the RLA chamber and the formation of internal barriers. Positive result is unchanged plug-in parts I-V characteristics and diode regulator 4 to 5 orders of - and + 1 V. The integration of Ge NPs has led to a downward current flow.

Electroluminescence spectra clearly show the different character of the integrated a-Si:H layer deposited in the glass chamber deposition system optimized for RLA, see the inlet graph in the **Figure 2**. The deposition of the fine-grained crystalline structure with embedded Si NPs typical of the reference sample #1 was interrupted by the inclusion of the a-Si:H layer with intermittent deposition, the electroluminescence itself being extinguished. In this structure, Ge NPs are also brightly inactive.

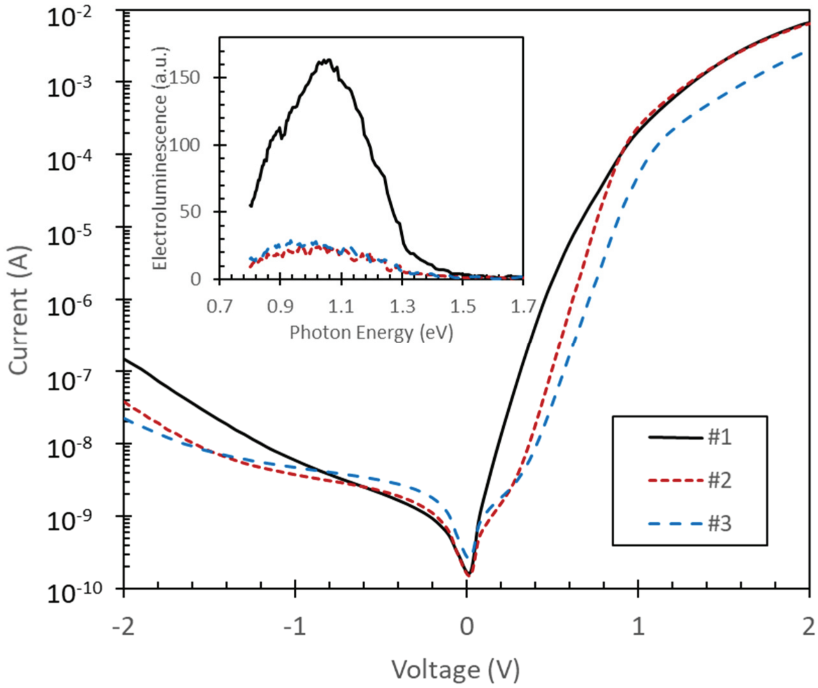

Figure 2 The dark volt-ampere characteristics of the reference sample #1, the sample #2 with the intrinsic a-Si:H thin film prepared in RLA chamber without embedded Ge NPs and sample #3 with the intrinsic a-Si:H thin film and embedded Ge NPs prepared in RLA chamber. The inlet figure shows the relative intensity comparison of the electroluminescence spectra measured in pulsed mode under forward current 3 mA.

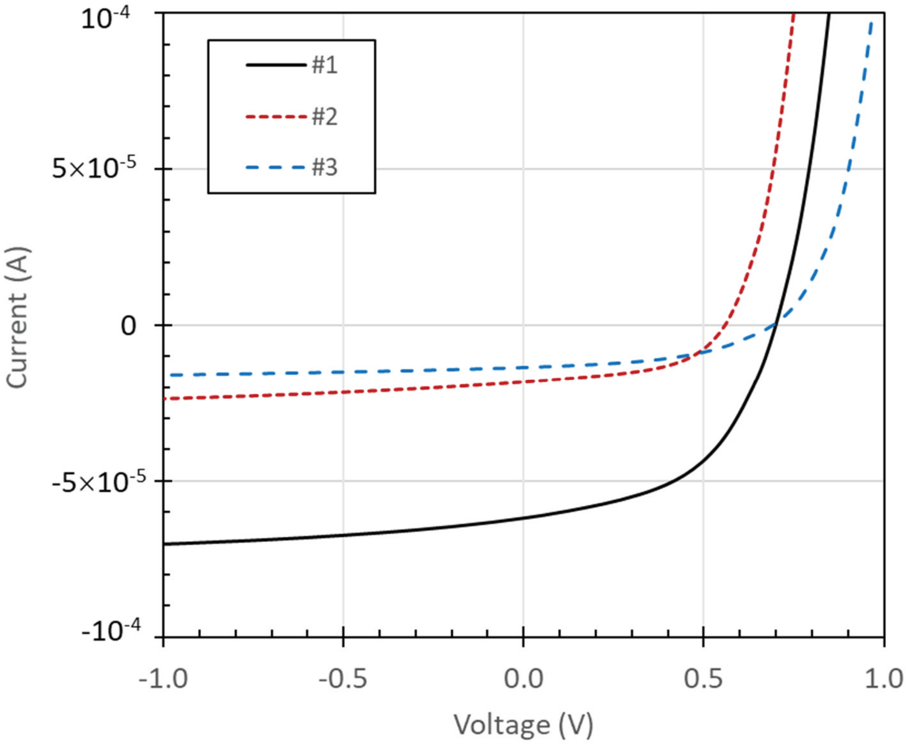

Figure 3 The volt-ampere characteristics of the reference sample #1 and the samples #2 and #3 (with embedded Ge NPs) under white light LED illumination with the total power density 100 mW/cm^2

The volt-ampere characteristics measured under white light LED illumination show the decrease of the photocurrent in samples #2 and #3 compared to the reference sample #1, see **Figure 3**. Thus, we conclude that the recombination defects are more related to the intermittent deposition of a-Si:H rather than to the integrated Ge NPs. We have also observed the decrease of the LED parallel resistivity by 3 orders of magnitude from about 100 MΩ in dark to about 100 kΩ under illumination.

4. CONCLUSIONS

Unlike the *in-situ* PECVD integration of Si NPs into a-Si:H layer in the stainless steal chamber, the integration of the Ge NPs into a-Si:H diode structures using RLA glass chamber did not demonstrate positive effects on increasing the efficiency of current diode structures, nor to any increase in radiant recombination on Ge NPs. The basic problem is the discontinuity of the deposition process of the entire layered diode, which leads to a significant influence on the structure of the undoped layer on the diode performance. Therefore we conclude that further research is needed to passivate the surface electronic states in Ge NPs to decrease the recombination of free carriers.

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