RELATION BETWEEN OPTICAL AND MICROSCOPIC PROPERTIES OF HYDROGENATED SILICON THIN FILMS WITH INTEGRATED GERMANIUM AND TIN NANOPARTICLES

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Abstract

The hydrogenated amorphous silicon layers (a-Si:H) were deposited by PECVD method on quartz substrates. During interruption of PECVD process the vacuum chamber was pumped up to 10^{-5} Pa and 1 nm thin films of Germanium or Tin were evaporated on the surface. The materials form isolated nanoparticles (NPs) on the a-Si:H surface. Then the deposited NPs were covered and stabilized by a-Si:H layer by PECVD. Those two deposition processes were alternated 5 times. The a-Si:H thin films with integrated Ge or Sn NPs were characterized optically by PDS and CPM methods, and microscopically by SEM and AFM microscopies. Optical and microscopic properties of the structures are correlated and discussed considering their application in photovoltaics.

Keywords: Thin films, a-Si:H, nanoparticles, Germanium, Tin

1. INTRODUCTION

Single solar cells based on hydrogenated silicon thin films show the highest efficiency of photovoltaic conversion for the mixed-phase structure (partly amorphous and partly microcrystalline) [1]. The amorphous phase is characterized by higher optical absorption coefficient in near infrared region, while the crystalline phase shows better electrical properties and high stability. However, its band gap is indirect, the absorption coefficient is lower and the final photovoltaic structure has to be thicker [2]. A way to increase the optical absorption coefficient is to integrate another kind of nanoparticles (NPs) with direct or near direct band gap to silicon structures. The Plasma Enhanced Chemical Vapor Deposition (PECVD) in combination with Vacuum Evaporation (VE) and Plasma Treatment (PT) was already demonstrated as convenient solution for the deposition of hydrogenated amorphous silicon (a-Si:H) thin films with integrated silicide NPs [3]. We have shown that the NPs embedded in a-Si:H thin film significantly enhance the near infrared optical absorption. The a-Si:H based diodes with embedded magnesium silicide NPs showed under illumination similar open circuit voltage and fill factor as diodes without NPs, but the defects induced by NPs deteriorated the short circuit current. In this contribution we present the combined technique as a suitable process for in situ depositions of diode structures based on a-Si:H with embedded Ge or Sn NPs. The possible application of such NPs to increase absorption in very thin a-Si:H films is discussed with a view of improving the efficiency of the resulting photovoltaic structure.

2. EXPERIMENTAL

A special setup with a home made vacuum chamber (**Figure 1**) allows to alternate both deposition processes, PECVD and VE from a Tungsten boat. For the deposition of a-Si:H thin films we used these parameters: flow rates of gasses: hydrogen 50 sccm, silane 2.36 sccm, (4.5 % of silane in mixture), pressure of gasses during the deposition 30 Pa, RF power 18 W for glow discharge excitation at the industrial frequency 13.56 MHz (size

of electrode: 62 x 62 mm^2, distance of electrodes: 32 mm) and deposition temperature 220 °C. The thickness of evaporated Ge or Sn was controlled by the Standard Quartz Crystal Sensor, typical thickness was 1 nm. Thin film structures were deposited on a fused silica glass substrates. Always two substrates were used for deposition of a-Si:H, one for the thin film with Sn or Ge NPs and one for the thin film without NPs which was used as reference. The deposition processes were alternated 5 times, the last deposition of NPs was not covered by a-Si:H. Final deposition process was evaporation of Titanium stripes with 2 mm distance as electrodes. **Figure 1** (on the right) shows a schematic of the final structure. This method was used to prepare samples 3K77, 3K78, 3K79, 3K80 with Sn NPs with different regime of hydrogen PT and sample 3K93 with Ge NPs. The deposited layers were characterized by scanning electron microscope (SEM) Maia3 FE-SEM (Tescan), high resolution transmission electron microscope (HRTEM) JEOL JEM 3010 (Japan) equipped with a thermo-emission LaB6 cathode and operated at 300kV. Surface topography was scanned also by an atomic force microscope (AFM) NTEGRA Prima (NT-MDT) by a Multi75E-G probe (BudgetSensors) in semicontact mode. The optical absorption coefficients of a-Si:H with embedded Ge NPs were measured by CPM - Constant Photocurrent Method [4] and with embedded Sn NPs measured by PDS - Photothermal Deflection Spectroscopy [5].

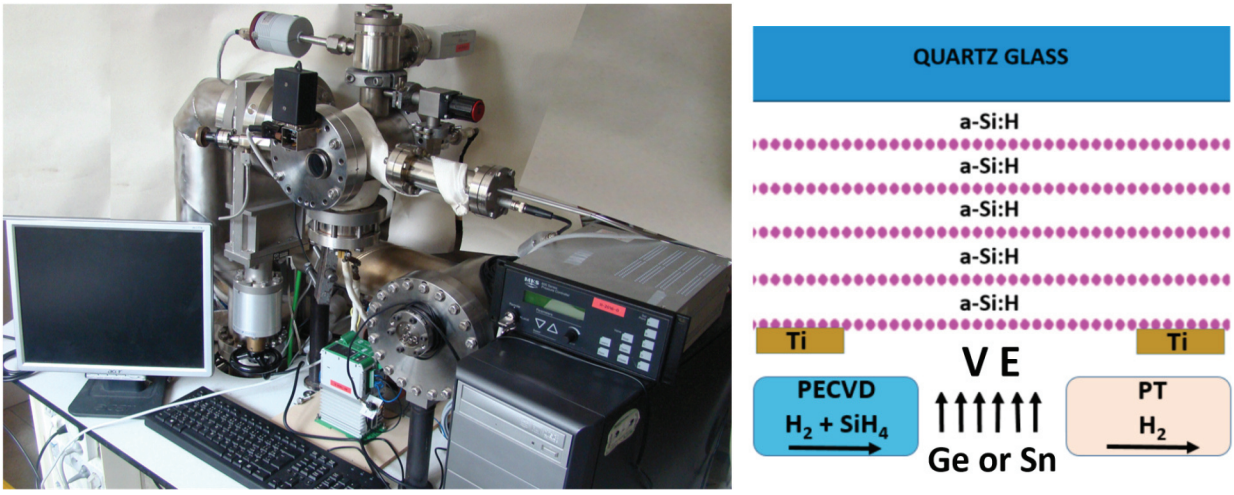

Figure 1 Deposition setup capable of alternation of two different deposition processes - PECVD and VE (on the left) and a schematic picture of requested structures of a-Si:H thin films with embedded Ge or Sn NPs (on the right).

3. RESULTS AND DISCUSSION

While a control structure of a-Si:H without NPs (**Figure 2a**) shows only fluffy 40 nm structures belonging to hydrogenated silicon, the picture of a-Si:H with NPs (**Figue 2b**) proves presence of Sn NPs with maximal size about 20 nm. HRTEM analysis of prepared films reveals that Sn is present in form of round nanoparticles with sizes in the range of approx. 4-10 nm. In the bright field (BF) images (**Figure 2c**) the Sn particles are displayed as darker spots on brighter a-Si:H film. Diffraction patterns (**Figure 2c**, in corner) obtained from the film show only week diffuse circles typical for amorphous material. The dark field (DF) image (**Figure 2d**) shows crystal origins with size 1-2 nm embedded in mostly amorphous material. Although for the recrystallization of the amorphous structures Si and evaporated metallic Sn we used high RF power for hydrogen PT the crystal NPs (like the one in **Figure 2b**) were observed rarely. That is why we could not prove any creation of the diamond respectively α-crystalline structure of the Sn NPs.

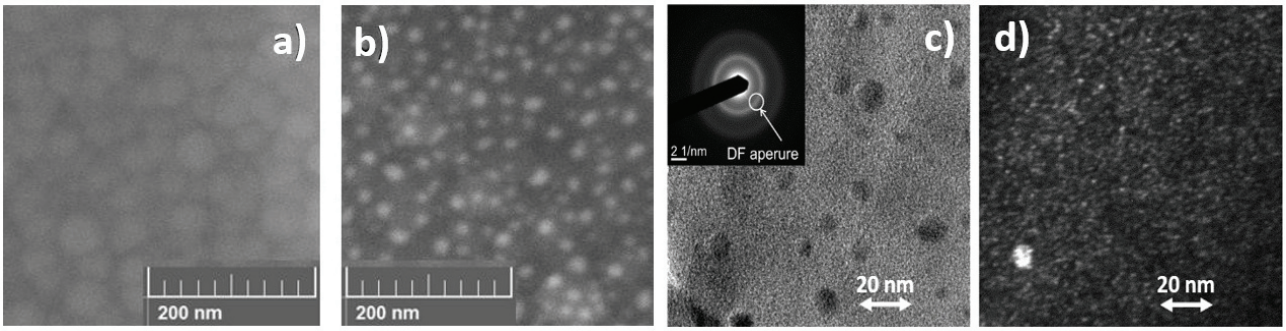

Figure 2 Typical SEM images of a) surface of a control a-Si:H film, b) a-Si:H thin film covered by Sn NPs, c) typical HRTEM BF image of a-Si:H with Sn particles on its surface, with corresponding diffraction pattern (inserted in corner), d) HRTEM DF image of the film. DF aperture used for d) is marked in the diffraction pattern in c).

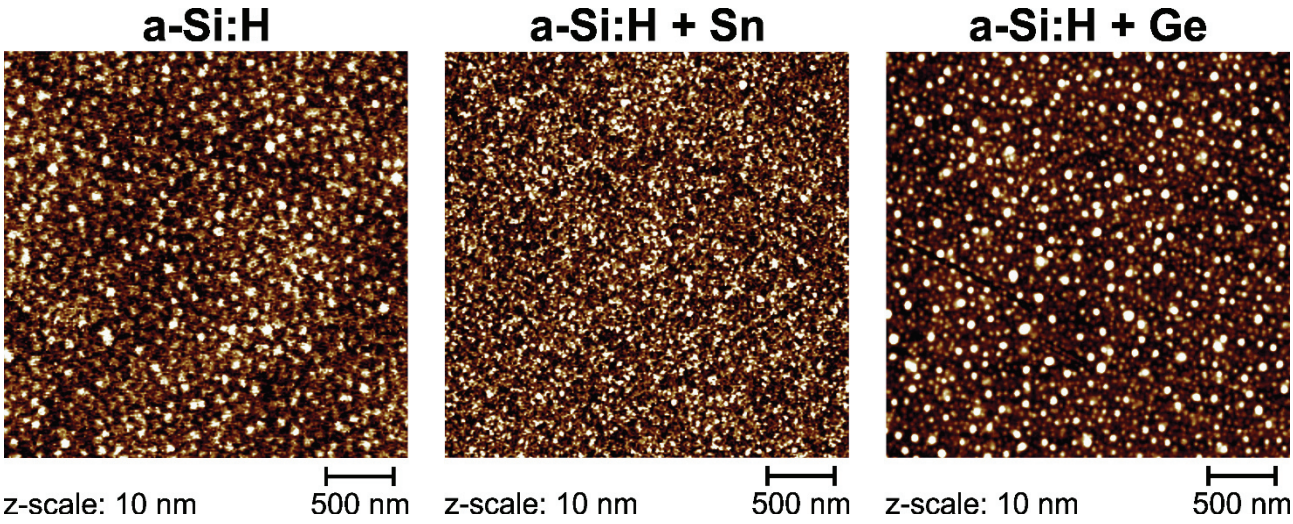

Figure 3 AFM surface topography of a) control a-Si:H,
b) a-Si:H with Sn nanoparticles, and c) a-Si:H with Ge nanoparticles

AFM surface topography of the control a-Si:H structure (**Figure 3**) corresponds well to the SEM image. The structure with Sn NPs is visually finer, yet the RMS roughness is slightly higher (3.4 nm) than in the case of the control structure (2.8 nm). Features on the surface of the structure with Ge NPs look similarly to the control sample and the RMS roughness is also the same.

Figure 4 shows the spectra of the optical absorption coefficients of a-Si:H with embedded Ge NPs (measured by CPM) and with embedded Sn NPs (measured by PDS). The absorption coefficient of a reference a-Si:H sample without NPs and of a crystalline silicon (c-Si) is displayed for comparison [6]. In the near infrared region the measurements show the optical absorption edge of a-Si:H that is for all thin films with encapsulated NPs shifted to lower energies together with an enhanced absorption. For proper comparison both samples (with and without NPs) deposited at the same time were treated by high energy RF Hydrogen plasma immediately after evaporation of NPs. For whole set of samples this process was repeated 5 times during deposition of non-doped a-Si:H thin film. The basic requirement for successful usage of embedded NPs is an increased absorption. However, NPs must not increase the number of defect levels in the amorphous structure. According to the measured results this requirement was successfully fulfilled for the sample 3K93 - for embedded Ge NPs.

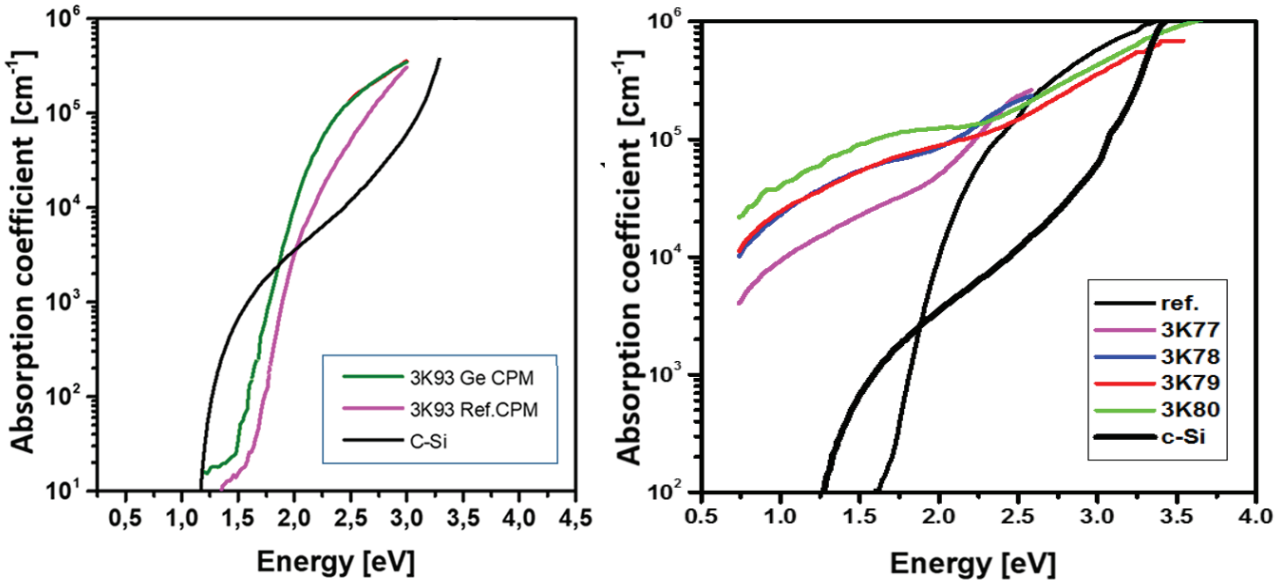

Figure 4 Spectra of the optical absorption coefficient a-Si:H thin films with and without embedded NPs. a-Si:H with and without Ge NPs (see the left picture) were measured by CPM. The right picture demonstrates absorption coefficient for thin films with and without embedded Sn NPs measured by PDS. Differences in dependences are given by different plasma treatment of deposited Sn NPs - see text. The absorption coefficient of c-Si in both pictures has been added for comparison.

For the set of samples with embedded Sn NPs the PDS measurements are significantly more sensitive than optical transmittance spectroscopy. The a-Si:H generally shows enhanced optical absorption in the visible light spectral region 1.9 - 3.4 eV compared to c-Si [6]. The exponential decrease of the optical absorption coefficient in a-Si:H at photon energies below 1.9 eV is related to tails of band-to-band electronic transition extended to band gap (Urbach edge). In the near infrared region below 1.5 eV the optical absorption coefficient is very low. Since there is the negligible optical absorption of the near infrared light, the quantum efficiency of the light conversion is also very low. Therefore, we have introduced the embedded Sn nanoparticles to enhance the optical absorption. **Figure 4** shows that the Sn NPs embedded in a-Si:H increase the optical absorption coefficient above 10^4 times. This means that the light is strongly absorbed already in thin film with thickness of 35 nm. As both SEM and AFM characterization revealed changes in surface features of sizes below 20 nm (far lower than visible or even near infrared light wavelengths), it is highly unlikely that such huge change in optical absorption originates in different surface scattering and is a result of the presence of NPs. The differences in the absorption in this spectral region between different structures with Sn NPs reflect a different hydrogen plasma treatment. The a-Si:H surfaces after interruption of PECVD deposition were exposed to different power of the PT: 100 W for sample 3k77, 33 W for 3k79, 66 W for 3K80. In the case of samples from 3K78 deposition the hydrogen PT was not applied.

4. CONCLUSION

In this contribution we demonstrate a possibility to integrate Ge or Sn NPs to intrinsic of a-Si:H thin films and to use this approach to increase the optical absorption in the films. The formation of Ge NPs in the amorphous structures, in the case of Sn NPs in metallic form, was confirmed by TEM measurements. The α-crystalline structure of the Sn NPs was not confirmed. We present the increase of absorption coefficient in visible part of light spectrum as well as a shift of the absorption edge toward lower energies. In the case of Ge NPs it is a needed prerequisite which can lead toward the requested increased efficiency of very thin PV diode structures of thicknesses only a few tens of nm.

ACKNOWLEDGEMENTS

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