

METALLIC AND SEMICONDUCTOR NANOPARTICLES INTEGRATED INTO THIN LAYERS OF HYDROGENATED AMORPHOUS SILICON OR SILICONCARBIDE

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Abstract

The combination of PECVD - plasma enhanced chemical vapor deposition and VE - vacuum evaporation at one vacuum chamber is in situ method how to integrate semiconductor (Ge) and metallic (Sn) nanoparticles into amorphous hydrogenated thin films and their structures on the base of a-Si:H or a-SiC:H. In this work we focus our effort to deposit a-SiC:H thin films from monomethylsilane (MMS = SiH₃-CH₃) diluted by hydrogen in the ratio 2/100 sccm. The Ge evaporates at vacuum higher than 2E-5 Pa. The TEM - transmission electron microscopy and AFM - atomic force microscopy are used for microscopical characterization of thin films while PDS - photothermal deflection spectroscopy and PL – photoluminescence spectroscopy are used for their spectroscopical characterization.

Keywords: a-SiC:H, MMS, Ge, Sn, nanoparticles

1. INTRODUCTION

This study builds on previous published results achieved on layered structures of amorphous hydrogenated silicon a-Si:H and non-stoichiometric amorphous hydrogenated silicon carbide a-SiC:H with embedded Ge nanoparticles [1]. In previous publications cited in [1], we have already described silane and methane diluted with hydrogen were used as the starting gases for PECVD. We have shown that the presence of methane in the ratio of 1:1 to silane in the discharge increases the carbon content in the deposited layers by only a few percent yet it shifts the transition from amorphous to mixed or even nanocrystalline layers while increasing the deposition temperature [1]. Using CPM, we have shown that these a-SiC:H films deposited in this way show a low amount of defects in band gap compared to a- μ c-Si:H films. It has already been confirmed in many past publications [2, 3] that it is not possible to simply increase the carbon content in the films for expanding the band gap of this semiconductor without increasing the methane:silane ratio. Another way is to use monomethylsilane - MMS, in which the carbon is already connected to the silicon by a chemical bond [4,5]. In line with the development trend of using highly temperature-stable SiC-based semiconductor devices, other deposition techniques such as HWCVD [6,7] or non-CVD techniques [8] are being tested. This work focuses on the possible use of conventional PECVD to modify the electrical and/or optical properties of a-SiC:H thin films by integrating Sn or Ge nanoparticles (NPs). Moreover, the formation of Ge NPs in thin films may be interesting not only for tuning the diode structures properties, but also for the study of their magnetic behavior [9,10].

2. EXPERIMENTAL

In previous publications ([1] and relevant references in [1]), we have already described different ways to integrate NPs into thin films and our custom-made system with a vacuum chamber, which allows to alternate two deposition processes - PECVD and VE without interrupting the vacuum - i.e. deposition *in situ*. For the deposition of a-SiC:H thin films we used the following parameters - flow rates of gasses hydrogen 100 sccm and MMS 2 sccm, pressure of gasses during the deposition 30 Pa, RF power 18 W for glow discharge

excitation at the industrial frequency 13.56 MHz and deposition temperature about 400°C. The thickness of Ge or Sn evaporated from a Tungsten boat was controlled by the Standard Quartz Crystal Sensor reporting typical thicknesses from 1 to 4 nm. Thin film structures were deposited on fused silica glass substrates or on Corning glass covered by FTO – tin oxide doped by fluor. Always a set of two substrates were used for deposition of a-SiC:H, one for the thin film with and the second without NPs. This second one was used as reference. The samples for TEM analysis were deposited simultaneously under the same conditions, but directly onto standard (commercial) Cu TEM grids covered by carbon foil. The deposited layers were characterized by scanning electron microscope (SEM) Maia3 FE-SEM (Tescan), high resolution transmission electron microscope (HRTEM) Tecnai TF20Xtwin (USA) operated at 200kV equipped with a field-emission gun (FEG) cathode and a high angle annular detector (HAADF) usable in the scanning TEM (STEM) imaging mode and an energy-dispersive X-ray analyzer for elemental analysis and mapping or profiling. Surface topography was scanned also by an atomic force microscope (AFM) NTEGRA Prima (NT-MDT) by a Multi75EG probe (BudgetSensors) in semi contact mode.

The setup for NIR PL spectroscopy uses the 10 mW blue LED (Thorlabs M470F2) triggered by pulse generator (typ. 37 Hz). To increase efficiency of collecting PL signal, the sample is illuminated perpendicularly from thin film side via a long-pass dichroic mirror (Thorlabs DMLP650R, 650 nm cut-on) and the same aspheric fused silica glass lens (focal length 25 mm, N.A. 0.5) that collects PL signal. The excitation and emission are spectrally purified by the OD6 band pass (Thorlabs FBH470-10) and long pass (Thorlabs FELH0550 and FELH0850) optical filters. Emitted PL light is spectrally analyzed using Horiba H20IR monochromator (600 gr/mm concave holographic grating) and focused by CaF₂ lens on an interchangeable Si and InGaAs photodiodes with built-in 2×10^{10} V/A ac amplifier (models 2151 and 2152, Newport Corp., USA), connected to a lock-in amplifier (Model SR830, Stanford Research Systems, Sunnyvale, California, USA) referenced to LED frequency. The spectral response was calibrated by a halogen lamp of known output followed by an additional correction [11].

The optical absorption coefficients were measured by PDS - Photothermal Deflection Spectroscopy. Photothermal deflection spectroscopy (PDS) measures directly the optical absorption of thin films on fused silica glass substrates with sensitivity of four orders of magnitude. The PDS spectrophotometer uses a 150 W Xe lamp as a light source and monochromator SpectraPro-150 equipped with two gratings blazed at 300 (1200 gr/mm) and 500 nm (600 gr/mm) operating in a broad spectral range from ultraviolet to infrared region 250–1400 nm. The sample is immersed in a transparent liquid and illuminated by monochromatic light with the probe laser beam passing parallel to the sample surface. The heat absorbed in the sample deflects the probe laser beam detected by the position detector and SR830 lock-in amplifier. Since the amplitude of the probe beam deflection is proportional to the optical absorption, the optical absorbance was evaluated by normalizing the signal on the deflection of the thin black film.

3. RESULTS AND DISCUSSION

Sn and Ge were evaporated on the a-Si:H and a-SiC:H thin films. The first control of deposited thin films on the thin films by AFM and SEM is shown in **Figure 1**. While in the case of Sn evaporation on the a-Si:H surface the creation of Sn NPs is very well visible by both AFM and SEM microscopies the evaporated Ge on the a-SiC:H thin film results in a smooth surface. The rms roughness is 0.83 nm, which is more than three times higher than the control without Ge (0.25 nm). It might indicate that Ge does not form crystalline nanoparticles, but an amorphous thin layer instead. This is supported by the characterization of TEM in **Figure 2**. TEM results obtained on the layered structure of a-SiC:H 9 nm / Ge 3 nm / a-SiC:H 9 nm deposited on a standard Cu grid demonstrated the amorphous character of the deposited films on the surface of a-SiC:H. Therefore, another way to achieve grouping of germanium into nanoparticles in crystalline form should be considered. We conclude that the amorphous substrate and temperature of 400 °C led to higher reactivity, especially germanium with surface silicon.

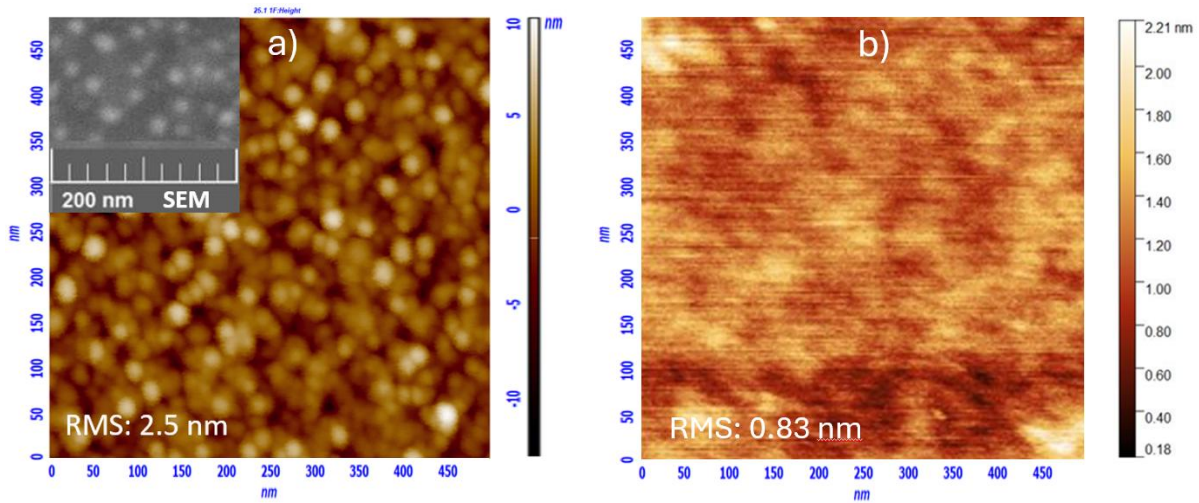


Figure 1 AFM imaging of Sn NPs vaporized on a-Si:H thin film at temperature of approx. 220 °C the insert is SEM imaging (a) and AFM imaging of Ge vaporized on a-SiC:H thin film at temperature of approx. 400 °C (b)

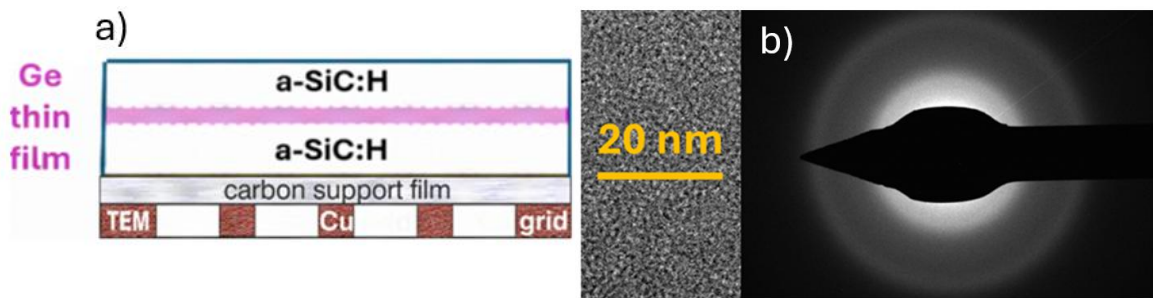


Figure 2 Sample structure prepared for TEM characterization (a) and observation result – bright field (BF) image and corresponding electron diffraction pattern (DP) typical for amorphous material (b)

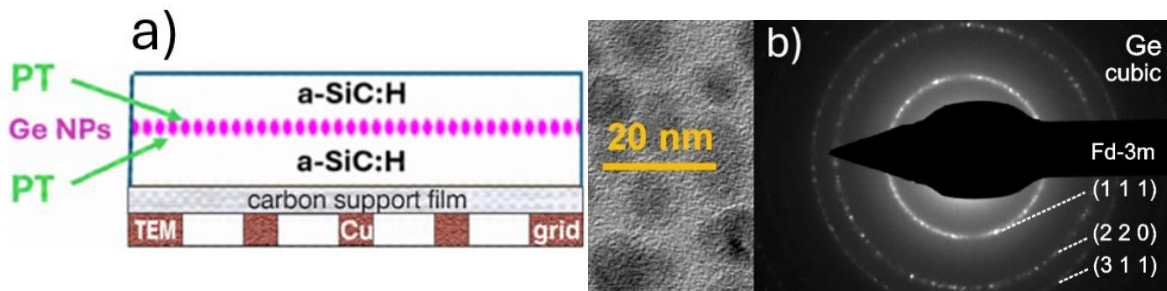


Figure 3 Sample structure prepared for TEM characterization (a) with indicated change in the deposition procedure, which is PT - plasma treatment before and after evaporation of the Ge layer and the result of observation, BF image and corresponding electron DP, assignable to the Ge crystal structure (b)

Because the reactivity of germanium with carbon is lower, we found a solution in the saturation of the surface with carbon using plasma treatment - PT. PT was successful using hydrogen with methane in a ratio of 100:2 [sccm] - see **Figure 3**, which confirms the crystalline structure of the NPs obtained in the manner specified above. Other more precise TEM and EDX characterizations have clearly demonstrated the grouping of germanium into nanoparticles with a crystalline structure. **Figure 4 a)** obtained in BF HRTEM mode shows a typical crystal NP with clearly visible lattice fringes. **Figures 4 b) – 4 f)** show a typical element profile which was obtained during analysis in the STEM mode, which is sensitive also to atomic composition and displays the observed NPs as bright, while the surrounding matter as dark (**Figure 4 b)**). The occurrence of Ge (see

Figure 4 f) is higher in the oval bright NPs, while between them drops to zero (see **Figure 4e**) – spectrum A from a dark place A). The Ge-K line intensity corresponds well with the signal of the HAADF detector depicted on the **Figure 4 d)**, whereas the Si-K line intensity is higher between NPs and at the particle place is lower but does not drop to zero. O and C do not show significant trends.

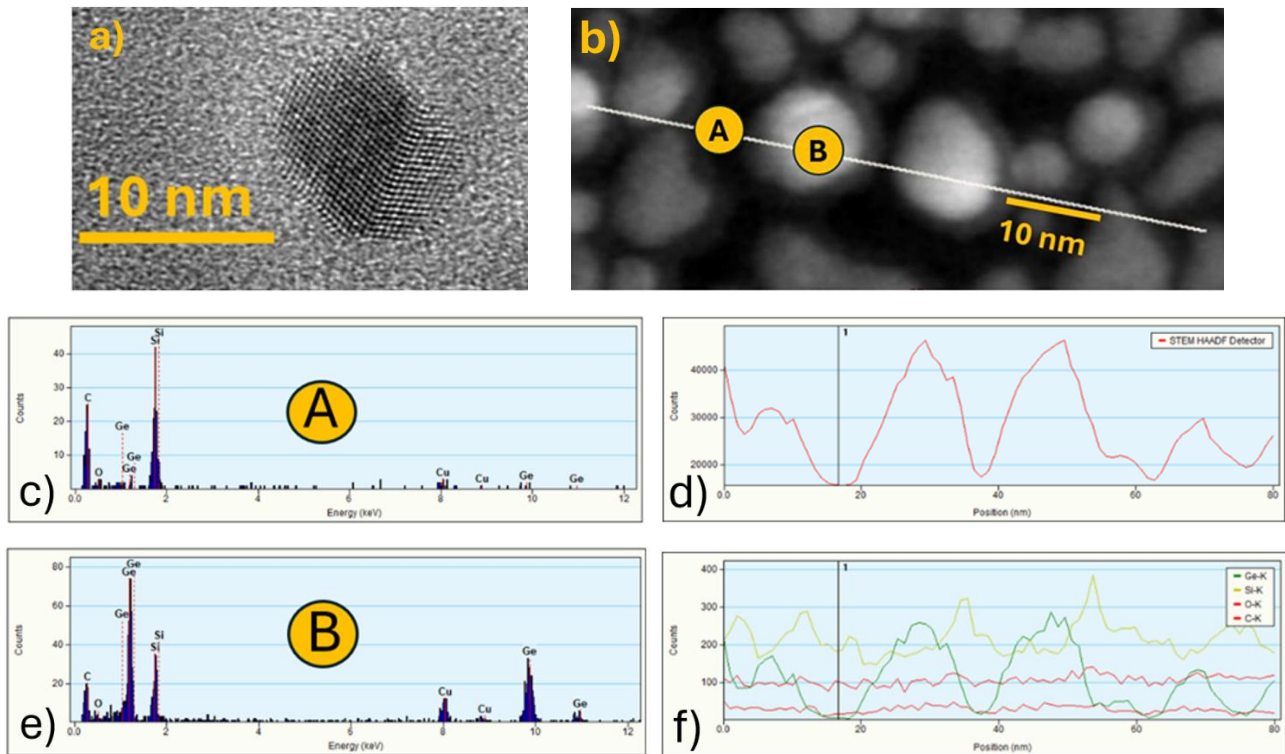


Figure 4 a): HRTEM (BF) image of a single Ge NP, **b):** STEM-HAADF image of a group of NPs with marking of the EDX profile line and two locations of EDX point spectra acquisition, **c):** EDX point spectrum from point A, **d):** HAADF detector intensity corresponded to profile line marked at **b)**, **e):** EDX point spectrum from point B, and **f):** occurrence of elements (depicted as intensity of character X-line of the given element) along the profile line: green, yellow, red or orange lines correspond to Ge, Si, C or O, respectively. The elemental profile was obtained on an 80 nm line with a 1 nm step, 1 EDX spectrum from each point, spectral range 0-40 keV, 20 eV/channel, 4000 ms acquisition time.

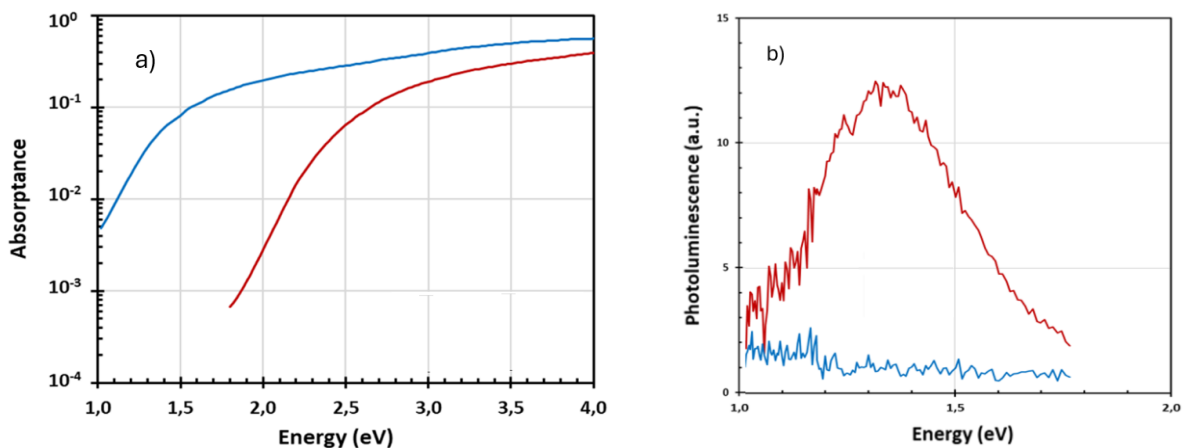


Figure 5 PDS measurements showed an increase in absorption and shifting of the absorption edge to lower energies **(a)**, PL measurements reveal the intrinsic photoluminescence of the a-SiC:H film and the negative effect of deposited Ge NPs **(b)**

For optical measurements, PDS and PL see **Figure 5.**, the structure of a-SiC:H / Ge / a-SiC:H / Ge / a-SiC:H / Ge / a-SiC:H with thicknesses of 9 / 3 / 9 / 3 / 9 / 3 / 9 nm was deposited on a quartz substrate and for comparison an a-SiC:H layer with a total thickness of $4 \times 9 = 36$ nm. The intrinsic a-SiC:H thin layers are highly transparent in NIR spectral region and exhibit NIR PL band with the maximum at 1.5 eV. The weak PL in a-SiC:H films is related to radiative recombination on defects in the band gap of a-SiC:H.

We attribute the decrease of PL to the non-radiative recombination of photoexcited free carriers in Ge sub-layers. Thus, we can conclude that the incorporation of Ge in a-SiC:H thin layers extend the absorption spectrum into the near-infrared region, which is beneficial for capturing more IR light and increasing photocurrent sensitivity. However, the decrease in intrinsic PL shows that Ge acts as a non-radiative recombination center. The mechanism of recombination to Ge NPs and the possibility of achieving electroluminescence as in the case of diode structures [9] are the subject of further investigation.

4. CONCLUSION

While increasing the deposition temperature over 300 to 350 °C for hydrogenated silicon alone leads from an amorphous structure to a mixed to microcrystalline structure, this limit exceeds temperatures over 400 to 450 °C if the layer is deposited from a mixture of Silane and Methane. The role of hydrogen gas dilution and the applied RF power also have a significant effect on the temperature for the transition from the amorphous to the microcrystalline phase. When using monomethylsilane (MMS - SiH₃-CH₃) the situation is similar, yet it should be also supporting the formation of one-dimensional Ge NPs in the crystalline form within the still amorphous SiC:H layer. However, the increased deposition temperature to 400 °C is also causing the increase in reactivity between the a-SiC:H surface and vaporized Ge. Germanium does not form separate islands on the surface, but a continuous amorphous layer. However, the used plasma treatment using methane diluted with hydrogen and therefore the assumed weak carbonization of the a-SiC:H surface leads back to the grouping of the vaporized germanium and to its crystalline structure.

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