THE DEPOSITION OF GERMANIUM NANOPARTICLES ON HYDROGENATED AMORPHOUS SILICON

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Abstract

We reveal the mechanism of Ge nanoparticles (NPs) formation on the surface of the hydrogenated amorphous silicon (a-Si:H) deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD) on ITO and a on boron doped nanocrystalline diamond (BDD). The coating of Ge NPs on a-Si:H was performed by molecular beam epitaxy (MBE) at temperatures up to 450 °C. The Ge NPs were characterized by Raman spectroscopy, scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM). The nanocrystalline Ge particles are conglomerates of nanocrystals of size 10-15 nm and quantum dots (QDs) with size below 2 nm embedded in amorphous Ge phase. After coating with Ge NPs the a-Si:H thin films show better adhesion on BDD substrates then on ITO substrates.

Keywords: Ge nanoparticles, a-Si:H, PECVD, MBE

1. INTRODUCTION

We Thin film semiconductor structures based of hydrogenated amorphous silicon (a-Si:H) are widely used for low cost and large area fabrication of optoelectronic devices, such as solar cells, light emitting diodes, sensors, etc. [1]. On the other hand, nanocrystals and quantum dots are nanometer-scale semiconductor structures that represent one of the most intensively developing areas of modern semiconductor physics. In the last few years, the efforts have been aimed to increase the efficiency of optoelectronic devices by embedding various nanoparticles (NPs) into the un-doped intrinsic layer [2–4]. 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. The later can be achieved using different types of QD passivation [5]. Our interest in this work is focused specially on the self-formation of Ge nanocrystals on a-Si:H surface. Therefore we combine the Plasma Enhanced Chemical Vapor Deposition (PECVD) and Molecular Beam Epitaxy (MBE) to prepare hydrogenated amorphous silicon (a-Si:H) thin films coated NPs.

2. EXPERIMENTAL

The boron-doped nano-crystaline diamond (BDD) films were deposited on fused silica substrates by Microwave Plasma Enhanced Chemical Vapor Deposition technique. Prior to deposition substrates were

seeded by spin-coating method using a colloidal dispersion of size 4-6 nm detonation diamond particles (NanoAmando, Japan). The diamond layers were grown in a diluted CH_4 (0.5 %) in H_2 plasma with addition of trimethylboron as boron precursor gas with a B/C ratio of 1000 ppm. The thickness of obtained BDD films was in the range of 150–170 nm. The deposition temperature was monitored during growth by a Williamson Pro92 dual-wavelength pyrometer [6].

The a-Si:H films were grown using the PECVD method from a monosilane (SiH_4) diluted in hydrogen (final mixture 8 % of SiH_4) at a temperature of 220 °C on glass substrates covered indium tin oxide (ITO) thin film and in second case we used Titanium grid covered by BDD as a conductive substrate. The pressure in chamber was kept at 70 Pa and density of RF power was about 0.01 W/cm^2 at 13.56 MHz for excitation of glow discharge. The film thickness was controlled by the deposition time and is about 300 nm. The Ge layers were deposited *ex–situ* in Novosibirsk using molecular beam epitaxy (MBE) on a-Si:H heated resistively by electric current passing through ITO or BDD layer. The MBE deposition technique was performed under Ultra High Vacuum (UHV) conditions, which allows the preparation of Ge NPs in non-hydrogenated form.

The analysis of phase and elemental composition of deposited Ge-Si hetero-structures was carried out by In-Via Renishaw Raman microspectrometer equipped by 442 nm HeCd laser (with intensity of < 1 mW on the sample to prevent local sample heating), more details can be found in Ref. [7].

The surface morphology was observed using Scanning Electron Microscopy (SEM) MAIA3-TESCAN. Detailed morphological analysis including imaging, electron diffraction and elemental analysis was carried out on a high-resolution transmission electron microscope (HRTEM) JEOL JEM 3010 operated at 300 kV (LaB6 cathode, point resolution 1.7 Å) and equipped with an EDS detector Oxford Instruments INCA Energy. Images were recorded on a Gatan CCD camera with resolution 1024 × 1024 pixels using the Digital Micrograph software package. The electron diffraction patterns was processed using the ProcessDiffraction V_7,3,2Q software developed by J. Lábár [8–10] and JCPDS PDF-2 database, International Cetre for Diffraction Data, release 54, 2004.

3. RESULTS AND DISCUSSION

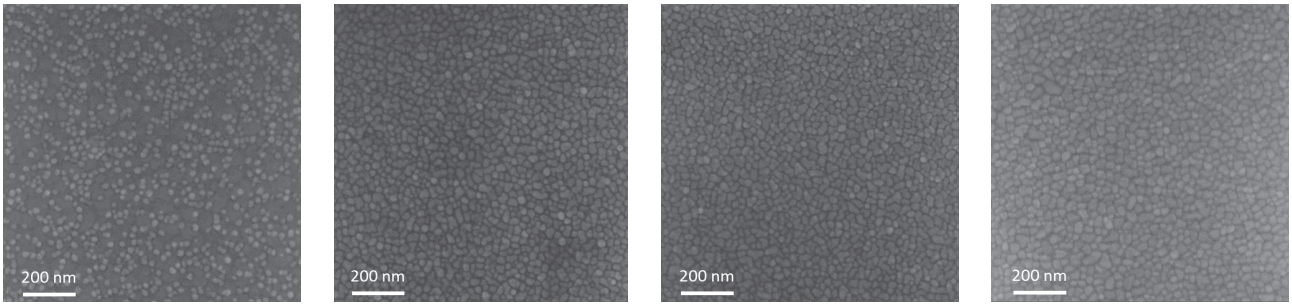

Figure 1 The SEM image of the smooth thin film a-Si:H/ITO coated by Ge NPs at 300, 350, 400 and 450 °C (from left to right)

The SEM image of the smooth a-Si:H surface coated by Ge NPs at temperatures 300, 350, 400 and 450 °C is shown in **Figure 1**. The Ge NPs diameter is in the order of few tens of nm for all deposition temperatures. At deposition temperature of 350 °C and higher we observe higher density of Ge NPs compared to lower deposition temperature.

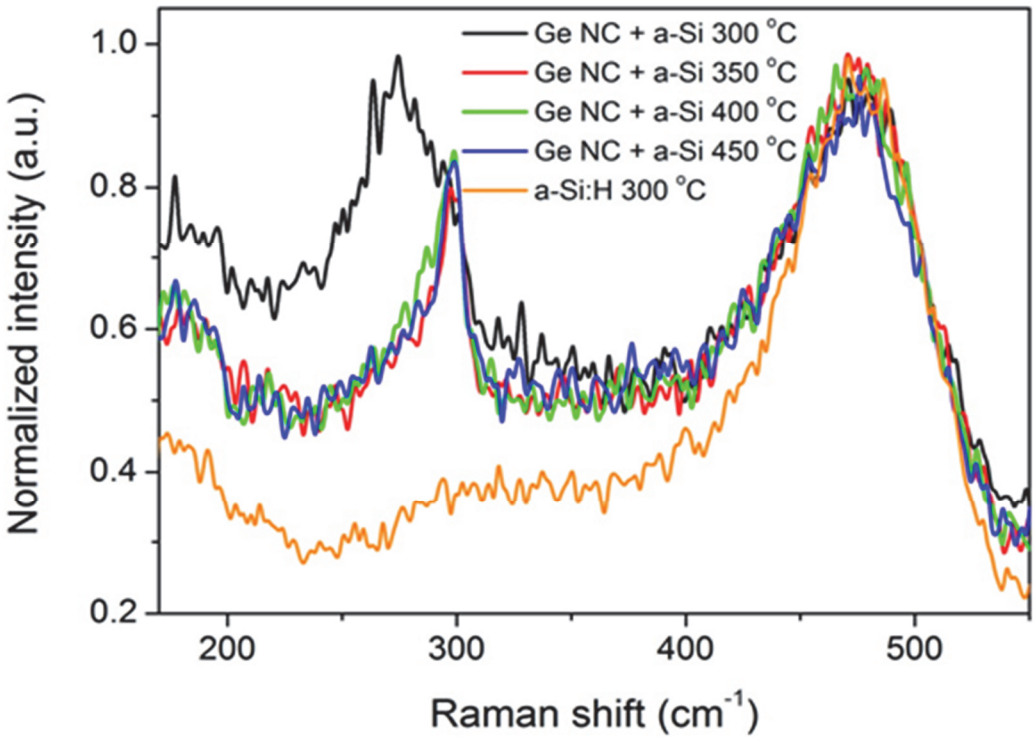

Figure 2 The Raman spectra of Ge NPs on a-Si:H/ITO layers

Figure 2 Raman spectra of Ge NPs prepared by the PECVD and MBE technique

Figure 2 shows the Raman spectra of Ge NPs on a-Si:H/ITO layers. Signal was detected for 60 s, no background subtraction or other treatments ware applied. Broad band around 480 cm^{-1}, detected for all samples in this series, is associated with amorphous silicon. The same signal was detected for all control samples, i.e. a-Si:H with no Ge content, see for example the orange spectra for a-Si:H film annealed at 300 °C. No nanocrystalline silicon content was detected even for silicon films annealed at temperature of 450 °C [11]. Broad amorphous germanium band situated at 270 cm^{-1} and weak nanocrystalline side band at 300 cm^{-1} was found for sample prepared at the lowest annealing temperature of 300 °C (black spectrum) [12]. At higher temperatures Raman spectroscopy proves germanium nanocrystalline nature of all films, without measurable amorphous germanium content. It means that temperature of 350 °C is sufficient to create fully nanocrystalline germanium particles. Thus, the optimum temperature is 350 °C, because higher temperature leads to evolution of hydrogen followed by the degradation of a-Si:H [13].

HRTEM bright field images show dark spots with size in the order of several tens of nm on light background, see **Figure 3**. The Energy Dispersive Spectroscopy (EDS) analysis reveals the presence of Ge only in dark spots, not in light background. Dark field images of Ge NP deposited at 350 °C reveal crystal particles of size 10-15 nm and nanoparticles with size below 2 nm homogeneously spread in amorphous matrix, see **Figure 4**. Comparison of bright and dark field images confirms that both of these particles are Ge particles present in particles which are imaged as dark spots on **Figure 3**. The electron diffraction confirms the amorphous character of Ge NPs deposited at 300°C whereas the electron diffraction patterns of Ge NPs deposited at 350°C and higher temperature shows clear diffraction spots arranged in diffraction circles that corresponds to cubic Ge, see **Figure 4**. Thus, the Ge particles deposited at 350°C or higher observed in SEM and the bright field HRTEM are conglomerates of nanocrystals of size 10-15 nm and very small nanocrystals with size below 2 nm embedded in Ge amorphous phase

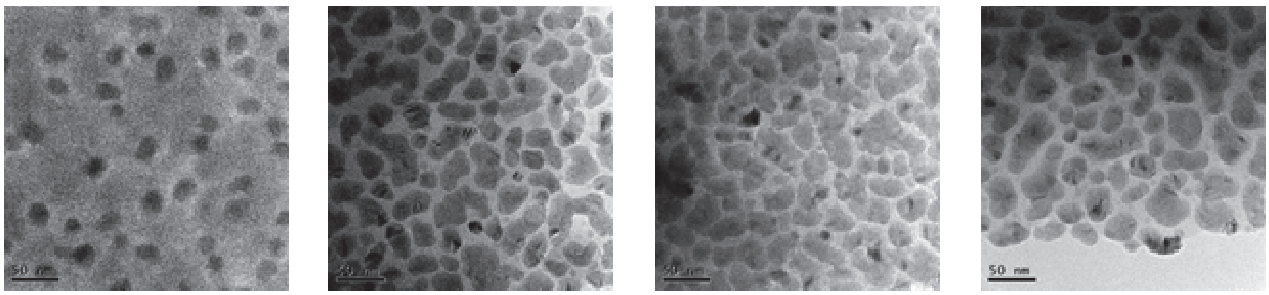

Figure 3 The HRTEM bright field morphology of Ge NPs on a-Si:H layer/ITO deposited by MBE at 300, 350, 400 and 450 °C (from the left to right)

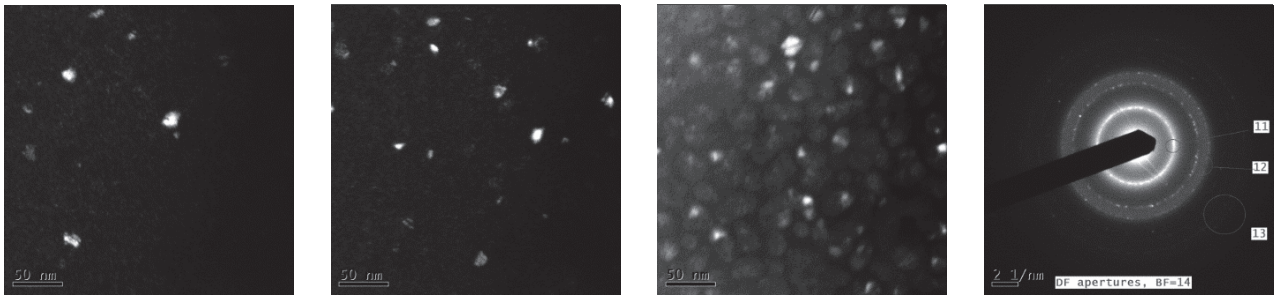

Figure 4 The HRTEM dark field morphology of Ge NPs on a-Si:H layer/ITO deposited by MBE at 350 °C (from the left to right aperture 11, 12, 13) and the electron diffraction pattern (right image)

During the Ge NPs growth the substrate was heated resistively by electric current. This process leads to peeling off the a-Si:H layers deposited on ITO whereas the a-Si:H layers deposited on semiconducting boron-doped nano-crystalline diamond showed better adhesion, see **Figure 5**. The SEM image shows BDD nanocrystals with grain size of c.a. 150 nm as well as the presence of the Ge NPs aggregates of tens of nm size.

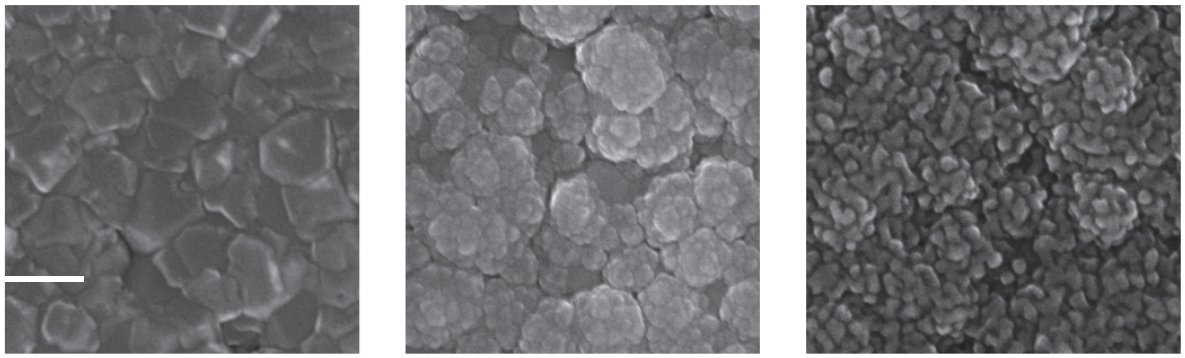

Figure 5 The SEM image of the thin film BDD (left) coated by a-Si:H (middle) and Ge NPs (right)

4. CONCLUSION

The technological processes PECVD and MBE have been successfully used for the deposition Ge NPs on the a-Si:H thin films. Morphology of the deposited Ge-NPs was observed by SEM, TEM and Raman spectroscopy. We found that optimum deposition temperature to form nanocrystalline Ge particles on the surface of a-Si:H thin film is 350 °C. The Ge NPs are conglomerates of nanocrystals of size 10-15 nm and quantum dots (QDs)

with size below 2 nm embedded in amorphous Ge phase. The a-Si:H thin films coated by Ge NPs shows better adhesion on BDD/glass substrates than on ITO coated glass.

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