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New method of porous Ge layer fabrication: structure and optical properties

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Abstract. Porous germanium films were formed by selective etching of the GeO_2 matrix from the $GeO_2\langle$Ge-NCs$\rangle$ heterolayer in deionized water or HF. On the basis of investigations by Raman spectroscopy, IR-spectroscopy it was supposed that a stable skeletal framework from agglomerated Ge nanoparticles (amorphous or crystalline) was formed after the etching of $GeO_2\langle$Ge-NCs$\rangle$ heterolayers. The kinetics of air oxidation of amorphous *por*-Ge layers was investigated by scanning ellipsometry. Spectral ellipsometry allowed estimating the porosity of amorphous and crystalline *por*-Ge layers which was 70 and 80%, respectively.

Introduction

Porous Si and Ge films are a topic of intense interest owing to their unique optoelectronic and morphological properties, as well as biocompatibility characteristics. The porous structure plays important role in the origin of the visible photoluminescence from these indirect bandgap semiconductors at room temperature [1]. In the last several decades, most researchers have concentrated on porous silicon [2]. Germanium is another important group IV semiconductor, which has a higher Bohr excitonic radius in compared with Si. So this allows the excitons to confine in the higher sizes of nanostructures, and quantum size effect should be stronger. However, it is still a challenge to produce porous Ge films with uniform structure on different material in a simple way.

1. Experimental and Results

We study composite material — $GeO_2\langle$Ge-NCs$\rangle$ heterolayers, consisting of glassy GeO_2 matrix with spheroid Ge nanoclusters embedded in it (Fig. 1a). We are able to obtain either GeO_2 films with Ge nanocrystals (higher deposition temperatures), or GeO_2 films with amorphous Ge nanoclusters (lower deposition temperatures). By means of structural and chemical modifications, $GeO_2\langle$Ge-NCs$\rangle$ heterolayers can convert into the unique coatings promising for application in nanoelectronics, photonics and other fields [3]. One of these modifications was removal of the GeO_2 matrix from $GeO_2\langle$Ge-NCs$\rangle$ heterolayer in deionized water or HF. So the released Ge nanoclusters agglomerated, forming a highly porous coating (*por*-Ge) on the substrate. The surface morphology of the porous Ge films was characterized by scanning electron microscope (SEM) and atomic force microscope (AFM). According to SEM (Fig. 1b) and AFM data, the porous Ge films had developed surface micro-morphology. Annealing of the *por*-Ge films or protection by a suitable cap layers improved their adhesion to various substrates.

On the basis of HRTEM, Raman and IR-spectroscopy it was supposed that a tough pomegranate-like structure from agglomerated Ge nanoparticles was formed after the etching of $GeO_2 < \langle$Ge-NCs$\rangle$ heterolayers. Moreover, an atomic structure of Ge clusters (amorphous or crystalline) was not changed when removing the GeO_2 matrix. In the Raman spectrum of *por*-Ge layer there was a broad band at 280 cm^{-1}, corresponding to an amorphous Ge phase (Fig. 2, spectra 1,2). Annealing

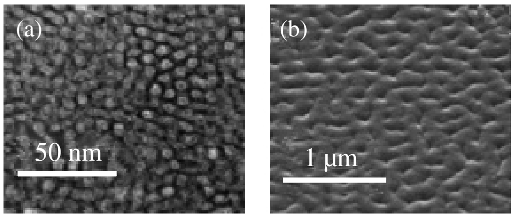

Fig. 1. (a) HRTEM image of Ge nanocrystals into GeO_2 matrix; (b) SEM image of the surface morphology of porous Ge film protected by the SiO_xN_y cap layer.

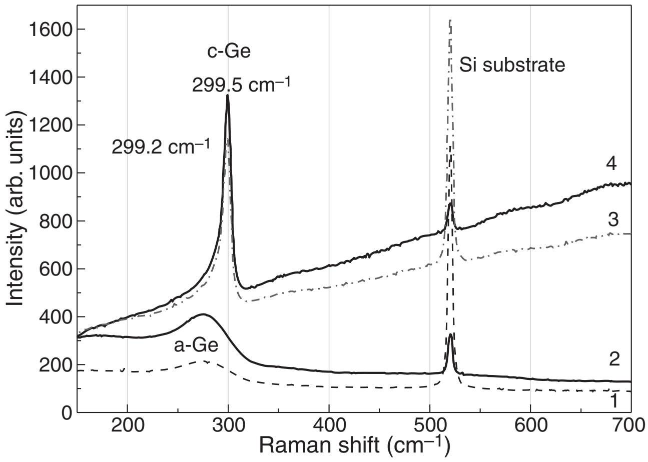

Fig. 2. Raman spectra of porous Ge film recorded in areas of sample with different thickness: 1,2 — before annealing; 3,4 — after annealing at 620 °C for 8 minutes in inert atmosphere.

of *por*-Ge layer at $T = 620$ °C led the sharp peak to appear at ~ 299 cm^{-1} due to scattering on optical phonons confined in Ge nanocrystals (Fig. 2, spectra 3,4). It is known that the Raman peak position provides information not only on phase state but on size of Ge nanocrystals. One can estimate that in our case the average size of Ge nanocrystals is 5–6 nm [4]. When Ge nanocrystals were formed, in addition to Raman scattering, a weak photoluminescence (PL) from laser excitation ($\lambda = 514$ nm) was observed in long-wave region. PL was registered as gradual increase of the Raman intensity from 320 cm^{-1} toward higher frequencies (Fig. 2).

Scanning ellipsometry ($\lambda = 632.8$ nm) revealed that optical properties of $GeO_2\langle$Ge-NCs$\rangle$ heterolayers and *por*-Ge lay-

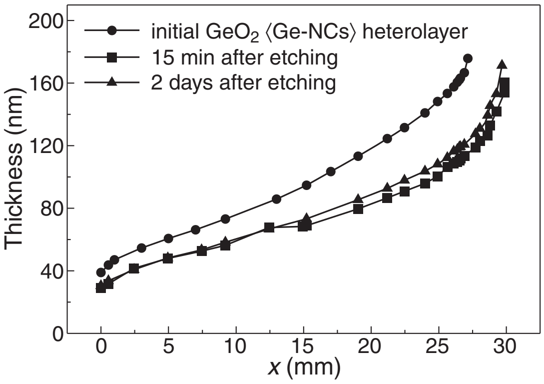

Fig. 3. Variations in thickness of GeO_2⟨Ge-NCs⟩ heterolayers after the GeO_2 matrix removal and further air oxidation of amorphous *por*-Ge layers (x — coordinate along sample).

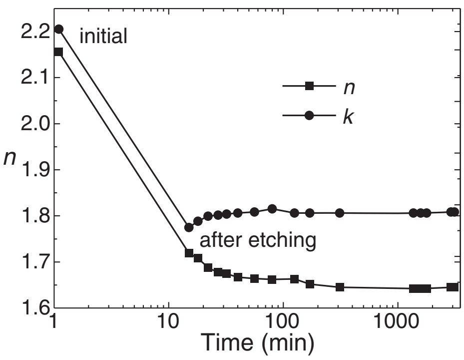

Fig. 4. Variation in optical constants of GeO_2⟨Ge-NCs⟩ heterolayers after the GeO_2 matrix removal and further air oxidation of amorphous *por*-Ge layers.

ers were homogeneous on a large area of substrate. It was obtained that the shrinkage of GeO_2⟨Ge-NCs⟩ heterolayer after the GeO_2 matrix removal (in deionized water for 30 s and in HF for 10 s) was 20–30% when scanning of the film with thickness profile (Fig. 3). Also the kinetics of air oxidation of amorphous *por*-Ge layer was investigated. If the amorphous *por*-Ge layer is left to age under ambient conditions for two days, then its thickness increases by 1–10% (Fig. 3). Variations in optical constants of GeO_2⟨Ge-NCs⟩ heterolayers after etching and exposure in the air are shown in Fig. 4. The removal of a considerable mass of GeO_2 matrix from the heterolayers led to an abrupt decrease of its optical refractive and absorption indexes. Further small increase in absorption coefficient indicates a gradient of air oxidation of Ge nanoclusters in the porous layer in depth.

Figures 5 and 6 show the spectral dependences of optical constants for amorphous and crystalline Ge nanoclusters before and after removal of the GeO_2 matrix from heterolayers (GeO_2 < ⟨Ge-NCs⟩). Double peaks appeared in spectra at 500–600 nm are typical for crystalline Ge (Fig. 6). One can see that the refractive index is reduced by approximately 0.7 for amorphous and by 0.4 for crystalline *por*-Ge layers in the range of $\lambda = 250-900$ nm when etching of the GeO_2 matrix. This is due to the fact that the refractive index of GeO_2 exceeds the air index. Variation in the absorption index for the film with amorphous Ge nanoclusters after GeO_2 matrix removal is more significant than for the film with crystalline ones. This is probably because of different degree of the film shrinkage

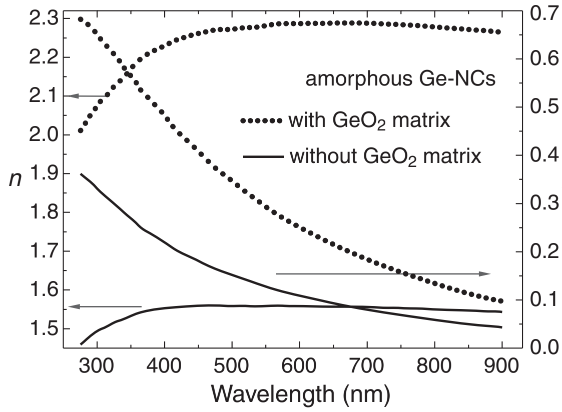

Fig. 5. Spectral dependences of optical constants for amorphous Ge nanoclusters before and after removal of the GeO_2 matrix from GeO_2⟨Ge-NCs⟩ heterolayers.

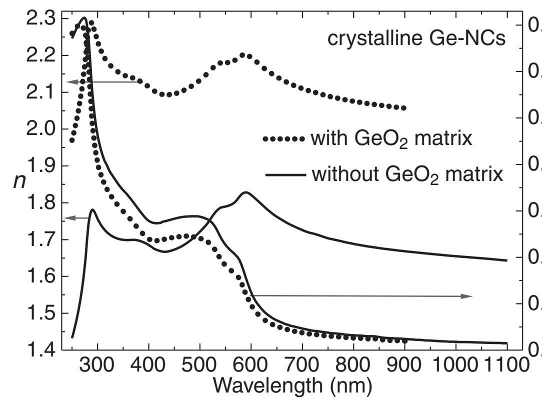

Fig. 6. Spectral dependences of optical constants for crystalline Ge nanoclusters before and after removal of the GeO_2 matrix from GeO_2⟨Ge-NCs⟩ heterolayers.

after this structural and chemical modification. Application of spectral ellipsometry with Bruggeman model allowed obtaining the porosity of amorphous and crystalline *por*-Ge layer, which was 70 and 80%, respectively.

2. Conclusion

In summary, we proposed a simple, reproducible method of formation of *por*-Ge layers on different materials. Complex of research methods revealed that a stable pomegranate-like structure from agglomerated Ge nanoclusters (amorphous or crystalline) was formed after the removal of the GeO_2 matrix from GeO_2⟨Ge-NCs⟩ heterolayers. Using structural and chemical modifications, Ge based oxides can transform into diverse layers which drastically differ in their properties (atomic structure, electrical, optical, mechanical *et al*).

Acknowledgement

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