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Ion beam induced endotaxial silver nanostructures in silicon

Puspendu Guha [a,b], Juluri Raghavendra Rao [a,c], Parlapalli Venkata Satyam [a,b,*]

[a] Institute of Physics, Sachivalaya Marg, Bhubaneswar 751005, Odisha, India
[b] Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai 400085, India
[c] Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Gustav Wieds Vej 14, 8000 Aarhus C, Denmark

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ABSTRACT

Coherently embedded structures in a crystalline substrate are known as endotaxial structures. In this paper, we report on the growth of silver (Ag) endotaxial structures in silicon using the aspects of both ion implantation and irradiation. In one case, endotaxial nanostructures of Ag at the Si interface are formed with 30 keV negatively charged silver ions (Ag^-) on $GeO_x/SiO_x/Si$ system. In another case, 30 keV Ag^- ions are used to create defects in GeO_x, SiO_x and in silicon substrate. Further deposition of a thin layer of Ag on irradiated $GeO_x/SiO_x/Si$ system yielded endotaxial Ag nanostructures relatively at lower temperature (700 °C) compared to the system without any irradiation effects. We also reveal that the irradiation effects with 1.8 MeV Ag^+ ions do not influence the early onset temperature of endotaxial nanostructure formation (unlike low energy ions). We show that it is essential to have crystalline silicon substrate to form Ag endotaxial nanostructures to grow endotaxial structures.

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1. Introduction

Nobel metal (Au, Ag, Pt) nanoparticles (NPs) are of great scientific significance in diverse technological applications, such as, optical, electrical and biological applications due to their plasmonic properties and large surface to volume ratio [1–4]. Among metal NPs, silver (Ag) shows highest electrical conductivity and is the best applicant for electrical characterization [5,6]; Ag is also the leading candidate for detecting organic dye-molecules, biomolecules via surface enhanced Raman spectroscopy (SERS) technique [7,8]. Embedded Ag nanostructures are known to be efficient for detecting the dye-molecules via SERS technique [9,10]. In general, nanomaterial synthesis and ion beam induced modification and their optical, electrical, magnetic properties have been studied [11–13]. Ion irradiation is used to generate variety of defects, which may induce structural deformation, phase change, strain etc., in the systems [14,15]. Earlier, we studied on the growth of coherently embedded endotaxial Ag nanostructures (NSs) in ambient conditions using chemical vapor deposition (CVD) [16] and physical vapor deposition (PVD) [9] techniques *without any use of ion beams*. Earlier reports suggests that the energetic ion beams have been useful to grow embedded metal nanostructures [17–19]. In these studies, volatile nature of GeO_x and SiO_x and Ag diffusion through these layers has been exploited to fabricate various size and shapes of coherently embedded (i.e., endotaxial) Ag nanostructures in crystalline silicon substrate with various orientations. The Ag NSs grown using above methods were used as SERS substrates to detect sub-micro molar dye-molecule, such as, crystal violet (CV) [9,10].

In the present work, we have focused on the ion irradiated effects of Ag ions (with 30 keV and 1.8 MeV ions) on $GeO_x/SiO_x/Si$ system to exploit the nature of defects formed during irradiation for enhancing the Ag diffusion to form endotaxial nanostructures besides the endotaxial nanostructures formation with the implanted Ag atoms. We have also compared these results with un-irradiated systems. Detailed surface morphological and interfacial diffusion aspects was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) experimental techniques.

2. Experimental

Commercially available silicon substrates with (100) orientation were first ultrasonically cleaned with acetone and then with alcohol for 5 min, each. Three systems with variable thickness of GeO_x layers, viz., ≈15 nm, ≈50 nm and ≈70 nm were deposited on silicon substrates by using physical vapor deposition (PVD) technique (chamber pressure $\approx 1.2 \times 10^{-6}$ mbar during the growth) at room temperature. A thin native oxide (SiO_x) (≈2–3 nm) is found to be present on Si(100) substrates, which usually

* Corresponding author at: Institute of Physics, Sachivalaya Marg, Bhubaneswar 751005, Odisha, India.
E-mail addresses: pvsatyam22@gmail.com, satyam@iopb.res.in (V.S. Parlapalli).

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acts as a diffusion barrier for overgrown layers on silicon substrates. The 15 nm $GeO_x/SiO_x/Si(100)$ substrates were first irradiated with 1.8 MeV Ag ions at room temperature at a particular fluence, 1×10^{15} ions/cm^2 using the 3.0 MV pelletron accelerator facility at Institute of Physics, Bhubaneswar (IOPB), India. This system with 1.8 MeV Ag ions is termed as *"high energy irradiation system"*. In another set of experiments, irradiations on 15 nm, 50 nm and 70 nm $GeO_x/SiO_x/Si(100)$ (at room temperature) under high-vacuum conditions ($\approx 5 \times 10^{-7}$ mbar) were carried out with 30 keV Ag ions at two fluences: 5×10^{15} ions/cm^2 and 2×10^{16} ions/cm^2 using low-energy ion implanter facility at IOPB. Hereafter, we will refer these systems as *"low energy irradiation systems"*. After both *high and low energy irradiations*, a Ag film of ≈2 nm thickness was deposited on the irradiated specimen using PVD system. In one set of irradiated specimen, no Ag film was deposited as this specimen is used to grow endotaxial nanostructures using 30 keV Ag implanted ions. To understand the onset temperature of the endotaxial formation, annealing was carried out at different temperatures (500–800 °C) for 30 min in ambient conditions.

Structural characterizations of all the samples have been carried out using field emission gun based scanning electron microscopy (FEGSEM) with 20 kV electrons (Neon 40 cross-beam system, M/S Carl Zeiss GmbH, Germany) and high-resolution transmission electron microscopy (HRTEM) with 200 keV electrons (JEM-2010, JEOL, Japan). For TEM observations, both planar and cross-sectional TEM specimens were prepared using conventional methods where preliminary thinning was carried out using abrasive materials (mechanical process) followed by ion milling process with low energy Ar ions (Ar^+).

3. Results and discussion

3.1. Un-irradiated system

Un-irradiated specimen (2 nm Ag/15 nm $GeO_x/SiO_x/Si(100)$) were annealed at 500 °C, 600 °C and 700 °C at ambient conditions and corresponding cross-sectional TEM micrographs are shown in Fig. 1(a–c). It is important to note that the substrate is crystalline in nature. No coherently embedded structures are seen on these systems even around 700 °C; however, only embedding of Ag nanostructures (and not endotaxy) could be seen at this temperature. But annealing them at 800 °C would enable to form endotaxial structures as shown in earlier reports [9,10]. Below, we show that similar results obtained for high energy irradiation systems as well (i.e., no endotaxy even at 700 °C: see Fig. 2) but with low energy irradiation systems, one can observe formation of endotaxial structures ≈700 °C (Figs. 6 and 10). One of the possible reasons for this could be due to large number defects (including displacements) with low energy ions resulting in enhancement of diffusion of Ag atoms from the deposited layer and these aspects are presented at later sections in the manuscript.

3.2. High energy irradiation systems

A ≈2 nm Ag thin film, deposited on the *high energy irradiated* samples at fluence 1×10^{15} ions/cm^2, were annealed at 600 °C, 650 °C and 700 °C for 30 min in air. Fig. 2(a–c) present low magnification planar TEM images for 600 °C, 650 °C and 700 °C cases respectively; insets of Fig. 2(a–c) display the corresponding low magnification cross-sectional TEM micrographs. Planar images show the formation of almost spherical Ag nanoparticles (NPs) with different sizes for 600 °C, 650 °C and 700 °C, respectively. We have observed the formation of Ag NPs just reaching the SiO_x/Si(100) interface at 600 °C (inset of Fig. 2(a)); at other higher temperatures, Ag diffusion towards the substrate is more (see insets of Fig. 2(a-b)). All the images in Fig. 2 clearly show no formation of endotaxial Ag NPs, while only embedded Ag NPs at 650 °C and 700 °C [9,16]. We haven't found any significant difference between irradiated (high energy) samples and normal samples (i.e., without irradiation), which is evident from the comparison of Figs. 1 and 2. It is to be noted that the projected range (R_p) of 1.8 MeV Ag ions in GeO_x/Si system is ≈780 nm (obtained using SRIM software [20]). Therefore, the defects formation is more around R_p (that is ≈780 nm for 1.8 MeV Ag ions) and hence there is no appreciable changes occurred and results are similar to un-irradiated systems. To understand the role of enhanced diffusion due to irradiation induced defects, we used 30 keV Ag ions and are discussed in the following section.

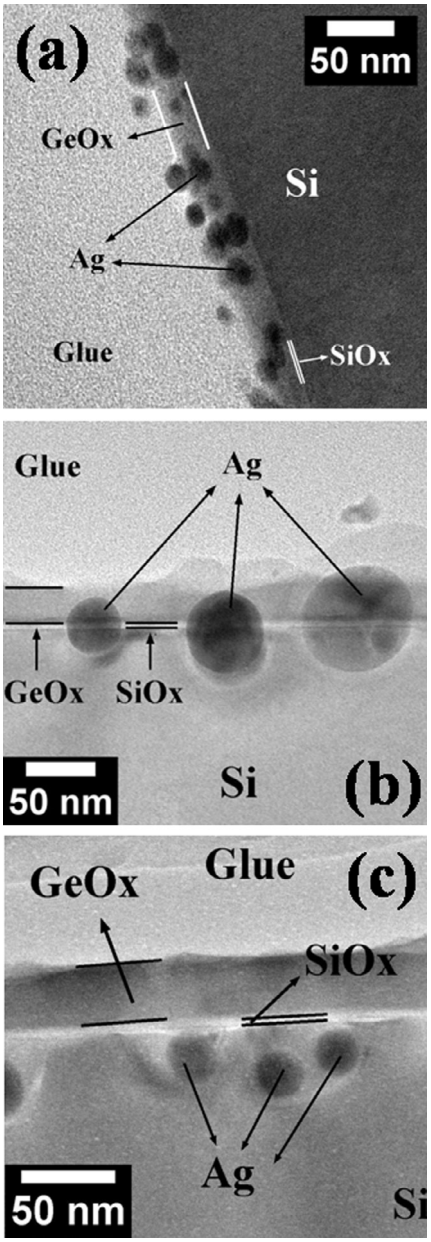

Fig. 1. Cross-sectional TEM micrographs of 2 nm Ag/15 nm $GeO_x/SiO_x/Si(100)$ (no irradiation) annealed at (a) 600 °C, (b) 650 °C and (c) 700 °C, respectively.

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