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Full Length Article

Growth of large aspect ratio AuAg bimetallic nanowires on Si(110) substrate

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ABSTRACT

Large aspect ratio bimetallic nanowire structures comprise potential applications in areas such as higher catalytic activity and surface Raman enhancement spectroscopy (SERS) substrates. By using the highly anisotropic ultra-clean Si(110) surface and with initial growth of sub monolayer (ML) Ag on such surface, a high aspect ratio AuAg bimetallic nanostructures can be formed. We report on the formation of large aspect ratio (>7.2 ± 0.8) AuAg nanowires on ultra-clean Si(110) surfaces using 0.5 ML Ag followed by 3.0 ML Au using molecular beam epitaxy (MBE) at a growth temperature of 300 °C. Under similar growth conditions without pre-deposition of Ag and only with deposition of 3.0 ML of Au consequences smaller aspect ratio (2.1 ± 0.1) monometallic Au nanostructures. The enhancement in aspect ratio of the nanostructures is attributed to the formation of one dimensional Ag layer (prior to Au growth) and Au-Ag bimetallic intermixing at elevated temperature. Considering deposition of 3.0 ML Au, a regime of substrate temperature ≈ 270–330 °C is found to be optimum to growth some of high aspect ratio (>25.0) AuAg nanowires as well. Exterior of this regime, at lower temperature due to low mobility of the ad-atoms and at higher temperature due to probable inter-diffusion of Ag, such extremely high aspect ratio AuAg nanowires found to be infrequent to grow. For growth at substrate temperature 300 °C, mean aspect ratio of the AuAg nanostructures is gradually increased in accordance with Au thickness up to 3.0 ML due to preferential accumulation of ad-atoms (Au, Ag) along Si⟨1$\bar{1}$0⟩ and thereafter reduces for adequate accumulation along Si⟨001⟩.

1. Introduction

In the diverge fields of nanotechnology, nanowires (NWs) are extremely important because of their implication as nanoscale interconnects [1,2], mesoscopic devices [3], laser [4], nanoscale optical waveguide [5] etc. Due to reduction of the dimension of metal particle to its electron scattering wavelength, many interesting, advantageous physical properties (plasmonic [6], magnetic [7], catalysis [8,9] etc.) are explored that are absent in their bulk counterpart. Metal NWs which comprise anisotropic electronic states along its one dimension than the other two orthogonal dimensions [10,11], withstand its applications in versatile areas, such as, hydrogen gas sensing by Pd NWs [12], field emission from cobalt NWs [13], glucose bio sensing using Au NWs [14] etc. In contrast with spherical shaped Au and Ag nanoparticles, one dimensionality of confinement of electron clouds consequence two distinct plasmon frequencies (known as longitudinal and transverse) for Au and Ag NW [15,16].

Combining two dissimilar metals at nanoscale in various methods give rise to formation of bimetallic nanoparticles (BMNPs) that can have many synergic effects. In many cases, such synergic effects become more advantageous than their monometallic counterparts such as catalysis [17,18], electrochemistry [19,20] etc. Among the different bimetallic pairs, Au-Ag combination shows remarkable miscibility in the entire window of variation of composition (Au:Ag ratio) [21–23] due to their isoelectronic configurations, nearly similar lattice constant with FCC structure and comparable surface energy. Indeed, Au-Ag bimetallic alloy nanostructures have superior catalytic activity for oxidation of carbon monoxide (CO) in

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fuel cells [24] and hydrogenation of dimethyl oxalate to methyl glycolate at low temperature as 418 K [25] than its monometallic counterparts. Using Au-Ag composite BMNPs in enzyme electrode, current response is largely enhanced in the β-D-Glucose and significant bio-sensing of glucose is achieved [26]. Surface plasmon resonance (SPR) property of Au-Ag alloy nanostructures is successfully tuned with gradual enhancement of Au:Ag concentration ratio [27]. SERS studies based on the SPR properties of Au-Ag bimetallic system, have been successfully implemented for substantial detection of 4-mer-captobezoic acid (4-MBA) [28] and Rhodamine 6G molecules [29]. Therefore, fabrication of Au-Ag bimetallic NWs on one dimensional template of ultra-clean Si surface could lead a step forward for advancement of application of metallic NWs in Si based technology, coupled with numerous synergic effects of BMNPs, in such areas as robust SERS substrates [30] and catalysts [18]. The effective SPR ranges for Ag and Au nanostructures are 400–470 nm and550–650 nm, respectively. For SERS with 633 nm excitation source, AuAg alloy structures on Si (5 5 12) found have larger cross-sections. Similarly, detailed understanding of ternary phase diagram i.e. *(Ag-Au)/Si* could lead to proficient usefulness of grown bimetallic AuAg nanoparticles on ultra-clean Si(110) substrate (in our present case) as a seed particle for preparing of Si nanowires.In our previous reports, we have investigated bimetallic AuAg growth on reconstructed vicinal Si(5 5 12) substrate with variation of metal (Au, Ag) thickness, annealing conditions to understand the growth mechanism and achieve optimum growth condition for formation of elongated nanowire along Si$\langle 1\bar{1}0\rangle$ direction [30,31]. For metal growth with sub monolayer coverage, reconstructed Si(5 5 12) substrate shows efficacy of formation of extremely large aspect ratio NWs due to preferential reactivity of tetramer rows along Si$\langle 1\bar{1}0\rangle$ and acting of grown step-terrace like structure as a barrier for diffusion along Si$\langle 66\bar{5}\rangle$, for the mobile ad-atoms [32–34]. But for larger thickness, over-layer growth consequences coalescence of smaller sized NWs along Si$\langle 66\bar{5}\rangle$ and adequate reduction of its aspect ratio. In this context, Si(110) substrate becomes very intriguing because of its utilization as a template for growth of extremely large aspect ratio NWs [35–37]. In those cases, enlargement of aspect ratio has been attributed as the combined effect of preferential mobility of the ad-atoms and facile reduction of interface energy along Si$\langle 1\bar{1}0\rangle$ than its perpendicular direction Si$\langle 001\rangle$. It is to be noted that, the larger aspect ratio implies a large number of surface atoms. Hence, nanowires would be more actively taking part in reactions, such as, catalysis.

In our present work, we have investigated growth of extremely large aspect ratio AuAg bimetallic NWs due to pre-modification of ultra-clean Si(110) substrate with sub monolayer Ag and thereafter Au deposition at substrate temperature 300 °C. Bimetallic AuAg growth has been compared with monometallic Au growth to elucidate the influence of Ag for formation of such AuAg NWs. We also present a systematic study of morphological evolution (in terms of mean aspect ratio) with variation of growth parameters i.e. substrate temperature (during Au growth) and Au thickness, to explore an optimum condition for AuAg bimetallic NW formation.

2. Experimental

We have used commercially available phosphorous doped Si(110) wafer with a resistivity 1–30 Ω-cm for growth of metal thin films. As a first step of preparing clean surface (i.e. native oxide free), sample is degassed at temperature 600 °C for 12–15 h under UHV. Then naturally grown native silicon oxide (SiO_X) layer (≈2 nm) from the top of Si(110) surface is removed using direct current heating method by repetitive flashing at 1200 °C for one minute. After that, it is slowly cooled down to desired temperature to carry out further experiments. Ag:Si(110) surface is prepared by deposition of 0.5 ML (One Monolayer ≈ 10 15 atoms/cm^2) Ag on clean Si(110) surface at room temperature (RT). The base pressure inside the MBE chamber is routinely maintained ≈2.0×10^{-10} mbar [38]. However, the pressure rises to ≈1.0×10^{-9} mbar during *'flashing'* process while removing the native oxide layer and during the thin film deposition. In Knudsen cell (K-cell), alumina and pyrolytic boron nitride crucible are used for evaporation of Au and Ag respectively. Thickness of the metal thin films is measured using a quartz crystal microbalance which has been calibrated for all the K-cells using Rutherford backscattering spectrometry method. Au and Ag are evaporated with flux rate as 0.50 ML/minute and 0.33 ML/minute, respectively. Substrate temperature is measured using a type K thermocouple which is attached in the backside of the manipulator. After the preparation of the sample it is brought in the ambient condition and morphology of the grown thin film (and nanostructures) is investigated utilizing field emission gun based scanning electron microscope (FEGSEM, NEON 440, Carl Zeiss GmbH) with electron beam energy 20 keV. Further imaging and energy dispersive X-ray spectroscopy (EDS) analysis have been carried out using a 300 keV scanning/transmission electron microscopy (FEI Technai, F30S/TEM) and 200 keV TEM (FEI – Talos FX 200). TEM specimens are prepared by mechanical polishing and low energy Ar^+ ion milling. To measure width (W) and length (L) of the nanostructures image analysis has been performed using ImageJ software (https://imagej.nih.gov/ij/). Magnitude of aspect ratio (*ar*) (i.e. L:W) is multiplied with corresponding probability (p) and summed over all its possible values i.e. $\sum ar \times p$ to obtain the mean aspect ratio ($\overline{ar}$) for various growth conditions of the nanostructures. Error bar to determine the mean values is calculated as$(ar_{max} - ar_{min})/2\sqrt{N}$, where ar_{max}, ar_{min} and N represent the maximum, minimum value of aspect ratio and number of nanostructures (under consideration for analysis), respectively.

3. Results and discussion

3.1. Comparison between monometallic Au and bimetallic Au-Ag growth

Fig. 1a shows SEM micrographs for growth of 3.0 ML Au on ultra-clean Si(110) substrate at substrate temperature 300 °C. Followed by the Au growth, Au/Si(110) system is annealed at 300 °C for 30 min. It depicts the formation of aligned array of elongated nanostructures reflecting the preferred anisotropic growth of nanostructures along Si$\langle 1\bar{1}0\rangle$ on ultra-clean Si(110) substrate. Following this, Au growth has been also performed on Ag pre-modified Si(110) substrate. Pre-modification of ultra-clean Si(110) substrate is done by deposition of 0.50 ML Ag on ultra-clean Si(110) substrate at room temperature (Ag:Si(110)). In this case, a 3.0 ML Au is deposited on Ag:Si(110) substrate at substrate temperature 300 °C. Followed by the Au growth, Au/Ag:Si(110) system is further annealed at 300 °C for 30 min. SEM micrographs for such Au-Ag growth on Si(110) substrate has been represented in Fig. 1b indicating formation of aligned array of elongated nanostructures. For such growth conditions, along with the formation of smaller aspect ratio nanostructures, extremely large aspect ratio (as large as ≈20.0) nanostructures are also formed. Fig. 1c represents the probability distribution of aspect ratio of the nanostructures: for a 3.0 ML Au deposited on ultra-clean Si(110) surface (orange colored in Fig. 1c) and on pre-deposited Ag on ultra-clean Si(110) substrate (blue colored in Fig. 1c). Comparison of these two systems indicates that, in terms of aspect ratio of the nanostructures, monometallic Au growth is relatively uniform. But, for Au-Ag growth, histogram of probability distribution becomes prominently broadened towards its tail with large magnitude of aspect ratio. Indeed, mean aspect