Available online at www.sciencedirect.com

ScienceDirect

Acta Materialia 79 (2014) 241–247

Acta MATERIALIA

www.elsevier.com/locate/actamat

Epitaxial growth of silver nanoislands on the surface of silicon nanowires in ambient air

Ren Lu, Yewu Wang *, Wei Wang, Lin Gu, Jian Sha *

Department of Physics & State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, People's Republic of China

Received 15 June 2014; received in revised form 11 July 2014; accepted 14 July 2014

Abstract

We study the epitaxial growth of Ag nanoislands on the surface of silicon nanowires (SiNWs) in ambient air by annealing SiNWs fabricated by metal-assisted chemical etching using Ag particles as the catalysts. We demonstrate that the nucleation of Ag on the surface of SiNWs is realized either by the direct decomposition of Ag_mO or by the reaction between Ag_mO and Si depending on the annealing temperature; Ag_mO is an adspecies with a lower effective detachment barrier, commonly introduced in oxygen-induced Ag surface migration systems. Along with the formation of Ag nanoislands, a thin layer of SiO_x is formed on the outside surface of Ag nanoislands. The ambient-air epitaxial growth of Ag islands on the surface of SiNWs offers great flexibility in designing ideal metal contacts and Schottky barrier formation, and studying the electronic, magnetic and optical properties of the Si/Ag system. We also believe that SiNWs decorated by Ag nanoislands have many potential applications in plasmonic photovoltaic cells, surface-enhanced Raman spectroscopy detection and electronic devices.

Keywords: Epitaxial growth; Silver nanoislands; Silicon nanowires

1. Introduction

Due to the unique electronic, magnetic and optical properties of the metal-on-silicon system, the growth of metal films on silicon substrates has been the subject of extensive studies over the past decades [1–5]. There has been much published research on the growth of Ag on Si surfaces, because of its prototypical nonreactive interface, which offers a promising application in ideal metal contacts and Schottky barrier formation [5–7]. The Ag/Si system also provides an opportunity to understand the mechanism of the epitaxial growth in systems with large lattice mismatch. In addition, Si nanowires decorated by Ag nanoparticles have recently attracted considerable attention, due to their potential applications in plasmonic photovoltaic cells [8], surface-enhanced Raman scattering [9–11] and biosensing [12]. Therefore, many methods have been developed to epitaxially grow Ag on Si surfaces, such as molecular-beam epitaxy (MBE) and magnetron sputtering [13–16]. As the presence of foreign atoms was expected to affect the growth dynamics and properties of deposited films by modifying the surface strain and crystalline properties, most of the Si surfaces were cleaned in ultrahigh vacuum (UHV) prior to Ag deposition [13,14,17,18]. Recently, epitaxial growth of Ag films on native-oxide-covered Si substrates using magnetron sputtering has been reported, demonstrating that oxide desorbs from the entire Si surface at ~550 °C [15,16]. It was believed that oxide desorption was caused by energetic bombardment of sputtered Ag particles, offering local oxide-free surfaces for epitaxial nucleation. However, all of the aforementioned methods have drawbacks,

* Corresponding authors.
E-mail addresses: yewuwang@zju.edu.cn (Y. Wang), phyjsha@zju.edu.cn (J. Sha).

http://dx.doi.org/10.1016/j.actamat.2014.07.030
1359-6454/

including vacuum, high energy consumption and long-term processing.

In this paper, we report the epitaxial growth of Ag nanoislands on the surface of silicon nanowires (SiNWs) by simply annealing Ag particles located at the bottom of SiNWs in ambient air at elevated temperature. The annealing temperature was found to have a great influence on the epitaxial growth of Ag nanoislands. More importantly, the epitaxial growth mechanism of Ag nanoislands on SiNWs in ambient air was explored and it was demonstrated that the nucleation of Ag on the surface of SiNWs is realized either by direct decomposition of Ag_mO or by the reaction between Ag_mO and Si, depending on the annealing temperature; Ag_mO is an adspecies with a lower effective detachment barrier, commonly introduced in oxygen-induced Ag surface migration systems.

2. Experimental methods

N-type, Sb-doped Si (100) wafers with a resistivity of 0.010–0.018 Ω cm were used for fabricating vertically aligned SiNWs by the metal-assisted chemical etching (MaCE) method [19–21]. Prior to chemical etching, silicon wafers were first sonicated in acetone, ethanol and deionized water sequentially, then immersed in concentrated H_2SO_4/30% H_2O_2 solution in a 3:1 volume ratio for 10 min to remove the organic contaminants and rinsed with deionized water, followed by an immersion in 2.4 wt.% HF aqueous solution for 30 s to remove the native oxide. The cleaned silicon wafers were immersed in 0.02 M $AgNO_3$/4.8 M HF solution for 30 s at 20 °C, obtaining Ag particles as the catalysts. The deposited Si wafers were then etched in 0.30 M H_2O_2/4.8 M HF solution for 15 min at 20 °C to fabricate SiNWs. Finally, the fabricated SiNWs (original SiNWs) were rinsed with deionized water and blow-dried in N_2. Uniform Ag nanoislands were epitaxially grown on the surface of SiNWs via a simple process of an annealing of Ag particles located at the bottom of the fabricated SiNWs at elevated temperature in ambient air. Morphology and microstructure investigations of the samples were performed by scanning electron microscopy (SEM; HITACHI S-4800) and transmission electron microscopy (TEM; JEOL JEM-1230). High-resolution TEM (HR-TEM) measurements and selected area electron diffraction (SAED) (JEM-2010 (HR)) were carried out to analyze the atomic structures and crystallographic orientations of SiNWs and Ag nanoislands.

3. Results and discussion

The surface of original SiNWs is very smooth, with large Ag particles (the catalysts, several hundred nanometers in size) located at the bottom, as shown in Fig. 1a and its inset. After annealing the samples at 550 °C in ambient air, Ag nanoislands appear on the surface of SiNWs. Fig. 1b and its inset are SEM and TEM images of the 60-min-annealed sample, which show that Ag nanoislands are uniformly formed on the surface of SiNWs with an average size of 9.1 nm, while large Ag particles located at the bottom disappear. The detailed morphological evolution of Ag nanoislands with annealing time is described elsewhere [22,23]. The HR-TEM image, as shown in Fig. 1c, indicates that Ag nanoislands are crystalline with a lattice spacing of 2.045 Å corresponding to Ag (200) planes, parallel to Si (400) planes with a lattice spacing of 1.361 Å. Although the lattice constants of Ag and Si are 4.09 and 5.43 Å, respectively, inducing a large misfit (24.7%), Narayan and Larson have reported that films grow epitaxially in the form of single crystals by domain matching epitaxy (DME), where integral multiples of lattice constants match across film–substrate interfaces, when the misfit is large relative to the substrate (>7–8%) [24]. In the Ag-on-Si system, a 4 × 4 mesh of Ag unit cells are well matched to a 3 × 3 mesh of Si unit cells, thus Ag may grow with cube-on-cube DME on the Si substrate with a low misfit of 0.4% [25]. Similar DME action has also been observed in Au-on-Si and Ag-on-GaAs systems [26,27]. Fig. 1d shows the SAED pattern of the wire shown in Fig. 1c. The Si pattern consists of spots, arising from diffraction from the (200), $(1\bar{1}1)$, and $(11\bar{1})$ planes, indicating that SiNWs fabricated by the MaCE method remain as single crystals. Ag shows diffraction from these same planes, and Ag (200), $(1\bar{1}1)$ and $(11\bar{1})$ planes are parallel to the Si (200), $(1\bar{1}1)$ and $(11\bar{1})$ planes, respectively: Ag(100)//Si(100), Ag $(1\bar{1}1)$ //Si $(1\bar{1}1)$ and Ag $(11\bar{1})$ // Si $(11\bar{1})$. Noting the parallel feature of the {011} family of crystallographic planes of both the Ag nanoislands and the SiNW substrate, the SAED pattern is strongly indicative of the Ag (100)[011]//Si (100)[011] in-plane epitaxial relationship of Ag-on-Si. Besides, these Ag nanoislands are characterized by two well-defined facets that correspond to the Si $(11\bar{1})$ and $(\bar{1}1\bar{1})$ planes, indicating their high crystallinity (Fig. 1c). Along with the formation of Ag nanoislands, a thin layer of SiO_x forms on the surface of Ag nanoislands. It has been demonstrated that these SiO_x caps are very effective in protecting the Ag nanoislands from aggregation and guaranteeing their thermal stability [22].

It is well known that oxygen-induced surface migration of Ag occurs when Ag particles are exposed to oxygen [28–30]. The addition of oxygen introduces an adspecies (Ag_mO) which can transport Ag between nanoislands more easily than Ag adatoms because of the lower effective detachment barrier of Ag_mO. The reaction at the surface of Ag particles can be written as:

$$2mAg + O_2(g) \rightarrow 2Ag_mO(g) \quad (1)$$

Usually, growth of Ag particles occurs by surface migration of Ag (in the form of Ag_mO) from small particles to large ones, known as Ostwald ripening [31–35]. Ag_mO molecules will decompose as soon as they impinge on the surface of other Ag particles because of the reversible oxygen attachment–detachment process, similar to the system