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Full Length Article

Annealing effects on electrical behavior of gold nanoparticle film: Conversion of ohmic to non-ohmic conductivity

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ABSTRACT

This paper reports on the electrical behavior of self-assembled gold nanoparticle films before and after high-temperature annealing in ambient environment. These films are made by depositing gold nanoparticles from a colloidal solution on glass substrates using centrifuge deposition technique. The current-voltage (I–V) characteristics of these films exhibits ohmic and non-ohmic properties for un-annealed and annealed films respectively. As the annealing time duration increases, the onset of non-ohmic behavior occurs at higher voltages. To understand the underlying mechanisms for the observed electrical conduction behavior in these films and how electrical conduction is effected by film morphology and structural properties before and after annealing, systematic comparative studies based on scanning electron microscopy (SEM), UV–vis absorption spectroscopy and X-ray photoelectron spectroscopy (XPS) have been performed. The morphology of the films shows that the assembled gold nanoparticles are distributed on the substrate in a random way before annealing. After 2 h annealing gold nanoparticles exhibit a higher filling fraction when examined by SEM, which means that they coalesce, upon annealing, with respect to un-annealed films. The UV–vis absorption spectra of the films show that there is a red-shift and broadening in the absorption band for the annealed films. The observed phenomenon is related to the plasmon near-field coupling effect and suggests that the nanoparticle ensembles interspacing has decreased. The structural and crystallinity of the films exhibit amorphous structure before annealing and pure crystalline phases with a preferential growth direction along the (111) plane after annealing. The XPS analysis further suggests the existence of the stable thin oxide layer in the phase of Au_2O_3 in the annealed films. The I–V characteristics have been described by Simmons' model for tunnel transport through metal-insulator-metal (MIM) junctions. The Fowler-Nordheim (F-N) plots show the transition of the in-plane charge transport mechanism from direct tunneling to field emission in annealed films. Our results suggest that, the formation of a thin layer of Au_2O_3, the proximity of the nanoparticles as well as their higher filling fraction are important parameters related with the tunneling process enhancement. The observed non-ohmic conductivity property can make these self-assembled gold nanoparticle films very useful structures in different applications such as sensing, resistors and other nanoelectronic applications.

1. Introduction

Recently, the interest in using metal nanoparticles deposited on semiconductor and dielectric substrates as a contact layer has attracted great attention. This is due to the relatively simple fabrication, low cost and a promise for large-scale integration in many optoelectronic device fabrication [1–6]. It has been reported that metal nanoparticle film properties can be tailored by controlling their morphology upon the evaporation and deposition processes such as electrochemical method [7], pulsed laser irradiation [8] and thermal annealing [9–13]. The post-deposition annealing at high temperatures has been suggested as an effective method for surface morphology modification with long-term stability. The annealing at different temperatures and time duration resulted in dramatic changes in surface morphology as well as structure properties of metal nanoparticle films [11–13]. The mechanism of the morphology transformation during annealing has been studied on the gold nanoparticle films deposited on a glass by in situ scanning transmission electron microscopy [14] and in situ optical spectroscopy [15]. These results show that gold nanoparticles deposited on a transparent substrate such as glass go through series of melting, inter-particle coalescence and dewetting processes. And for high-temperature annealing, the gold nanoparticles deposited on the glass gradually get embedded in the substrate resulting

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in strongly bonded and morphologically stable nanostructures for various applications such as sensors and optical devices [15–17]. In addition, detailed studies indicate that annealing at high temperature in air can also help the formation and stabilization of the gold oxide on the films in the presence of the substrate [18–23]. While, the optical and morphological properties of gold nanoparticle films after thermal treatment and annealing have been studied [10,12,14–17], a detailed investigation of high-temperature thermal annealing influence on their electrical conductivity properties of these films through a subsequent change in morphology and structure properties of the films is lacking.

A thorough understanding of the electrical conduction properties and charge carrier transport mechanisms for annealed metal nanoparticle films is essential for their possible use in various optical and electrical applications [3–6]. The electrical conductivity in the metallic nanoparticle films is a strong function of the nanoparticle ensembles size and interspacing as well as the thickness and continuity of the deposited films [24–27]. In general, the electrical conductivity of the metal films with a thickness smaller than the mean free path of their electrons is drastically reduced based on Fuchs –Sondheimer and Mayadas–Shatzkes theories [28–30]. Reasons for this reduction are mainly related to the scattering of the electrons from the surfaces and grain boundaries. Similar electrical conduction reductions have been also reported for metallic nanoparticle films [31–34]. The electrical conductivity may vary over many orders of magnitude if the film is transferred from electrically discontinuous to continuous film which depends on the metal filling fraction [27]. The mechanism of the charge transfer process in discontinuous metallic film is based on a charge carrier creation under applied voltages and transport of these charges among assemblies by tunneling has been proposed by Neugebauer and Web [35]. Recent works suggest that the tunneling probability can be voltage dependent under high voltage regimes and bistable switching also reported [36–39]. The dependence of the conductivity of discontinuous metallic nanoparticle films on temperature has been reported [40,41]. For very small particles and ultra-thin nanostructured films, <5nm, the electronic band splitting and electron confinement effects have to be considered which resulted in intrinsic semiconductor characteristic of clusters. In such nanostructures, the non-ohmic I–V behavior observed at low temperatures [41–43].

The present work characterizes the electrical properties of self-assembled gold nanoparticle films on glass substrate before and after high-temperature thermal annealing. The I–V characteristics, morphology and structure properties of these films are reported. A detailed analysis is discussed and suggests that the non-ohmic behavior in the electrical conductivity of the annealed gold nanoparticle film is related to the morphology and structural evolution and modification during the high-temperature annealing process.

2. Experimental details

2.1. Synthesis of gold colloid nanoparticles

The gold colloid nanoparticles are prepared by the sodium citrate reduction of $HAuCl_4$ in distilled water. Spherical gold nanoparticles with 15 nm in diameter are synthesized under reflux condition. The reflux environment is used to maintain constant density of gold nanoparticles in the colloid.

2.2. Substrate preparation

The adhesion of the gold nanoparticles on a glass substrate is improved by the substrate silanizations. First, the substrates are cleaned by ultra-sonication consecutively in ultra-pure water, ethanol, acetone, and ultra-pure water for 5 min. Then, glass substrates are immersed for at least 2 h with the typical piranha solution containing mixture of 3:1 concentrated 70% sulfuric acid to 30% hydrogen peroxide. They are rinsed with the deionized water and dried in an oven at the temperature of 80 °C. Finally, the substrates are silanized by the 3-aminopropyldiethoxymethylsilanefor 2 h and dried in the oven again.

2.3. Preparation and characterization methods of gold nanoparticle films

To deposit the gold nanoparticles on glass substrate, a prepared glass substrate of 1 mm thickness with area of $9 \times 22\ mm^2$ is placed in the gold nanoparticle colloid and is then centrifuged. During the centrifugation process, the nanoparticles accelerate toward the substrate and adhere to its surface. Few discontinuous self-assembled gold nanoparticle films on glass substrates are fabricated. These films are annealed at temperature for 500 °C for 2, 4 and 8 h in ambient environment. The surface morphology of these films are studied by a Hitachi SU3500 scanning electron microscope (SEM). The crystalline structure of these films are investigated by a PANalytical X-ray diffractometer (XRD) with high intensity Cu (Kα) radiation (λ = 1.5406 Å). X-ray photoelectron spectroscopy (XPS), by a Thermo VG scientific, VG multilab 2000, is used for the characterization of the nanostructure compositions. The optical absorption spectrum of these films is measured using a UV–vis spectrometer (Perkin-Elmer, lamda 25). The gold filling fraction factor calculated by Image J software and the current-voltage measurements are performed using DC-picometer (PHILIPS, PM-2436) for measuring current value through point contacts with 6 mm interspacing where an adjustable low noise DC power supply is used to apply voltage across the film.

3. Results and discussion

3.1. Electrical conductivity properties

Current-voltage (I–V) measurements are performed to investigate the electrical conductivity properties of the gold nanoparticle films before and after high-temperature annealing. Fig. 1 shows the current measurements for a wide range of voltages from 10 to 300 V in ambient environment for these films. The I–V curve of the un-annealed film has exhibited ohmic conductivity behavior and a linear dependence. While, the I–V curves for the films that have been annealed for 2 and 4 h exhibit a lower linear conductance for low voltage values and jumps to higher conductance for high voltages presenting a non-ohmic I–V characteristic. As is shown in Fig. 1, the conductivity of the film after 4 h annealing time is lower than that of 2 h annealed film. In addition, the onset of increase in conductance (i.e., nonlinear behavior) occurs for higher voltage values. After 8 h annealing time the films show a linear I–V behavior with a very low conductivity. The measured conductivity for un-annealed film is $\sim 6.7 \times 10^{-11}\,\Omega^{-1}$ and for the linear part of the annealed films the conductivity values are $\sim 6.1 \times 10^{-12}\,\Omega^{-1}$, $6.9 \times 10^{-12}\,\Omega^{-1}$ and $5.8 \times 10^{-12}\,\Omega^{-1}$ after 2, 4 and 8 h annealing time, respectively. The measured conductivity of the linear part of I–V characteristics for the films after different annealing time is approximately the same. These obtained values for the conductivity are few orders of magnitude smaller in value in comparison to the value reported for the bulk gold ($4.2 \times 10^6\,\Omega^{-1}$) [44]. This reduction as discussed earlier is associated with the discontinuity in the deposited films and small constitutive particle size of the film through the electron free mean path theory. Reduction in conductivities occurs due to the electron mean free