Journal of Alloys and Compounds 698 (2017) 400–409

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Designing highly conductive and stable silver nanocrystal thin films with tunable work functions through solution-based surface engineering with gold coating process

Mingi Seong [a], Seung-Wook Lee [b], Hyungmok Joh [a], Woo Seok Lee [a], Taejong Paik [c], Soong Ju Oh [a, *]

[a] Department of Materials Science and Engineering, Korea University, Seoul 02841, South Korea
[b] Department of Semiconductor Systems Engineering, Korea University, Seoul 02841, South Korea
[c] School of Integrative Engineering, Chung-Ang University, Seoul 06974, South Korea

ARTICLE INFO

Article history:
Received 15 August 2016
Received in revised form
9 November 2016
Accepted 13 December 2016
Available online 18 December 2016

Keywords:
Silver nanocrystal
Flexible electrode
Work function
Solution process
Gold coating
Galvanic exchange

ABSTRACT

We fabricated highly conductive and stable silver nanocrystal (Ag NC) thin film electrodes with tunable work functions using an all-solution-based method involving sequential ligand exchange and gold (Au) coating processes. We studied the effect of the Au coating process on the ligand-exchanged Ag NC thin films and successfully demonstrated the formation of a thin Au layer on the surface of the Ag NCs. We investigated the morphological, structural, optical, chemical, and electrical properties of the Ag NC thin films before and after Au coating. The work function of the electrodes was precisely controlled by varying the treatment time and concentration of gold chloride trihydrate ($HAuCl_4 \cdot 3H_2O$) solutions. The thermal stability of the Au coated Ag NC thin films in air was greatly enhanced, and an extremely low resistivity of 3.4 μΩcm was achieved. Taking advantage of this solution-based low-temperature process and using a minimal amount of Au for cost reduction, we fabricated all-NC-based high-performance flexible photodetectors.

1. Introduction

Flexible electronics are gaining increasing interest for various applications such as solar cells [1], transistors [2], circuits [3], light-emitting diodes [4], photodetectors [5], piezoactuators and piezo-transducers [6], etc. In particular, the metal electrodes in these electronic devices are essential core parts for all the device applications. Carbon nanotubes [7], nanowire networks [8], graphene [9], conductive polymers [10], indium tin oxide [11] and nanocrystals (NCs) have been used to fabricate flexible metallic electrodes. Among them, silver (Ag) NCs have received huge interest and have been studied extensively for applications in electronic devices owing to their relatively low cost and highest conductivity [12]. In addition, they can be fully solution-processed during their synthesis and fabrication [5–29]. Although Ag has the lowest resistivity of all the metals, the thin films made by Ag NCs are insulating as each Ag NC in the thin films is surrounded by insulating and long organic ligands, which are introduced during the synthesis. To remove these insulating organic ligands and increase the conductivity, many efforts have been made such as low temperature annealing [8,17], plasma sintering [18], photonic sintering [19], microwave annealing [20], laser sintering [21–26], chemical treatments [27,28], and ligand exchange process [29]. Especially, the ligand exchange process is one of the most promising methods, as it consumes very less time, can be carried out at room temperature in a solution medium, and does not need high-vacuum based processes or expensive equipment.

Although highly conductive Ag NC thin films have been made, the resistivity achieved with those films is still quite higher than that of bulk Ag. Moreover, the investigations and efforts to manipulate the work function of Ag NC thin films have rarely been conducted. Indeed, the work function of electrodes is very crucial for catalytic, electronic, optoelectronic, and photovoltaic applications as it determines the band alignment and barrier heights for charge carrier injection at the junctions. In order to facilitate the charge injection at metal-semiconductor contacts, the metal work function should be close to the conduction or valence band edge to

* Corresponding author.
E-mail address: sjoh1982@korea.ac.kr (S.J. Oh).

http://dx.doi.org/10.1016/j.jallcom.2016.12.157
0925-8388/

make Ohmic contacts with n-type or p-type semiconductors, respectively. For example, for a p-type semiconductor device which is the common case of solution-processed semiconductor of organic compounds [30] or some examples of solution processed NC semiconductors [31,32], a work function higher than that of Ag is generally required to inject majority carrier (holes) easily from the metal to the p-type semiconductor [33]. In addition, a higher work function is desired to prevent the oxidation of metal electrodes and achieve a high stability in air. Utilizing high work function metals such as gold (Au) or platinum (Pt) can address the issues of oxidation and stability, but they are expensive compared to Ag NCs. This is the reason why there are few reports on the fabrication of solution-processed Au or Pt NC thin films.

The thermal stability of electrodes in air is an important issue. Most of the electronic devices require a thermal annealing process during the fabrication. For solution-processable semiconductors, like some examples of organic materials, such as poly(3-hexylthiophene) [30,34] or NCs, a thermal annealing process is commonly needed to further enhance their electronic properties. Generally, in the case of flexible electronic devices, the annealing temperature should be lower than 250 °C to prevent the substrate damage. However, the solution processed Ag NC thin films, especially ligand exchanged Ag NC thin films, are readily oxidized and do not exhibit good thermal stability even at low temperatures (150–250 °C). This significantly limits the application of Ag NC thin films for fabricating high-performance flexible electronic devices.

Here, we developed a solution-based process involving sequential ligand exchange and Au coating processes to produce highly conductive electrodes with high and tunable work functions and high thermal stability in air. Since the overall properties of nanomaterials are largely determined by the surface state, we only modified the surface of the Ag NC thin films fabricated in this study with a thin Au layer using a galvanic exchange method [35]. We investigated the morphological, structural, optical, chemical, and electrical properties of the Ag NC thin films prepared by ligand exchange and Au coating. By utilizing successive ligand treatments on the Ag NC thin films and by coating their surface with Au, we could successfully modify their work function. The work function of the Ag NC thin films changed from 3.89 to 4.54 eV. Moreover, we achieved a resistivity as low as 3.4 μΩ cm, which is the lowest resistivity exhibited by electrodes fabricated below 100 °C. After the optimization, we obtained materials with low resistivity, high work function, anti-oxidation activity, and high thermal stability at temperatures up to 250 °C, using a minimal amount of Au. All of the syntheses, depositions, surface treatments, and Au coating processes were conducted using low-temperature solution processes, and were therefore compatible with a standard photolithography method and flexible substrates. Using the Au-coated Ag NC thin films, we fabricated all-NC- and all-solution-process-based photodetectors with p-type semiconductor of lead selenide (PbSe) NC thin films as the active layers without using the expensive vacuum-based techniques. This approach provides a pathway to fabricate cost-effective and high-performance flexible electronic devices.

2. Material and methods

2.1. Chemicals

Silver nitrate ($AgNO_3$) was obtained from Alpha Aesar. Oleylamine, oleic acid, toluene, ethanol, 3-mercaptopropyl trimethoxysilane (MPTS), acetone, isopropanol (IPA), octane, hexane, ammonium thiocyanate (NH_4SCN), methanol, Gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$), lead oxide (PbO), 1-octadecene (ODE), selenium (Se) pellets, trioctylphosphine (TOP), and diphenylphosphine (DPP) were obtained from Sigma-Aldrich. GXR 601 and AZ 300 MIF were purchased from AZ electronics materials. All of these chemicals and materials were used as received without further purification. Deionized (DI) water was produced by a Milli-Q-system.

2.2. Characterization

Transmission electron microscopy (TEM, Tecnai 20), scanning transmission electron microscope - energy dispersive X-ray spectroscopy (STEM-EDS, JEOL 2100F, Cs corrected), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX, Hitachi S-4300), and X-ray diffraction (XRD, Rigaku Model D) were used to characterize the morphological and structural properties of the Ag NCs. An X-ray photoelectron spectroscopy (XPS, Axis NOVA, Korea Basic Science institute) using a monochromatic aluminum (Al) Kα (1486.6 eV) radiation was used to analyze the elemental composition of the Ag NCs. The work function of the Ag NCs was measured using an ultraviolet photoelectron spectroscopy (UPS, Ultra DLD, Korea Basic Science institute) using a helium (He) I (21.2 eV) radiation. The optical properties of the Ag NCs were investigated by ultraviolet–visible (UV–Vis, Cary 5000) and Fourier transform infrared (FT-IR, Agilent Cary 630) spectroscopies. A probe station (MST-4000A) and a four-point probe (CMT-SR2000N) were used for measuring the electrical properties of the Ag NCs. Photocurrent measurements were conducted using a probe station (MST-4000A) combined with a white light emitting diode (Luna) as a light source.

2.3. Synthesis of 3.5 nm-sized Ag NCs

We synthesized the Ag NCs by using wet chemical methods [36]. Silver nitrate (1.7 g) was added to a mixture of 5 mL of oleylamine and 45 mL of oleic acid in a three-neck flask. The reaction mixture was heated to 70 °C and degassed for 120 min prior to heating in a nitrogen (N_2) atmosphere at 180 °C (at a heating rate of 1 °C min^{-1}). The reaction was stopped when the temperature reached 180 °C. After cooling in air to room temperature, toluene and ethanol were added to the mixture to precipitate the Ag NCs. The samples were centrifuged three times to obtain uniform-sized Ag NCs. After the last centrifugation, hexane was added and evaporated in a vacuum chamber to determine the exact mass of the Ag NCs. The solution was then placed in a vacuum chamber for 2 h, and then octane or hexane was added to the remaining Ag NCs in order to obtain a 100–200 mg mL^{-1} Ag NC solution.

2.4. Fabrication of Ag NC thin films

To deposit a self-assembled monolayer (SAM) on various substrates, the substrates were previously immersed in a toluene solution of 5% (by volume) MPTS. Prior to the treatment with MPTS, the substrates were washed in order with acetone, IPA, and DI water before being placed in a UV ozone cleaner for 30 min so that MPTS could be anchored to their surface. Glass substrates were used for carrying out the XRD, FT-IR, and UV–Vis analyses, Si wafers were used for performing the UPS, XPS, and SEM-EDX analyses, and polyethylene terephthalate (PET) substrates were used for fabricating flexible photodetectors.

After the MPTS treatment, the Ag NC solutions (in octane or hexane) were deposited on the substrates by spin-coating. The substrates were immersed in a 30 mM NH_4SCN solution (in methanol) for 2 min for ligand exchange. After the ligand exchange, the substrates were washed with methanol to remove excess ligands.