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Seed-layer-free growth of ultra-thin Ag transparent conductive films imparts flexibility to polymer solar cells

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ABSTRACT

In this work, by introducing Cu dopant, ultra-thin Ag transparent conductive films were prepared on glass and PET substrates without seed layers. The percolation threshold thickness for the Cu doped Ag thin films was as low as 6 nm with a RMS roughness only 0.19 nm. The prepared 6 nm Cu doped Ag thin films, Ag(Cu), had a transmittance of 80% at 550 nm and a sheet resistance of 14.1 Ω sq^{-1}. The Ag(Cu) thin films revealed excellent thermal, chemical, and mechanical stability. Flexible polymer solar cells using the Ag(Cu) electrode reached a convert efficiency of 7.53% with a very thin PTB7-Th:$PC_{71}BM$ active layer. The proposed ultra-thin alloy transparent conductive films are ease of fabrication and beneficial to light harvesting, which are promising for large-area applications in flexible photovoltaics.

1. Introduction

Ultra-thin metal films (≤ 10 nm) have attracted extensive attentions as transparent electrodes in flexible optoelectronic and photonic devices with the boost of flexible electronics [1–6]. It possesses the inherent advantages of metals such as excellent ductility, high conductivity, and high transmittance due to low optical loss in the visible and infrared range when the thickness gets down below the skin-depth thickness. Comparing with other ITO substitution candidates such as graphene, carbon nanotubes, Ag nanowires and conductive polymers, ultra-thin metal films feature cost-effective and large-scalable fabrication as well as high figure of merit. It is believed that the ultra-thin metal films are quite promising for flexible electronic application if ultra-smooth growth with a low percolation threshold and high stability is realized.

Ultra-thin Ag films were usually demonstrated by introducing a seed layer, which transferring a Volmer-Weber (3D island) growth mode of Ag thin films on glass substrates into a continuous 2D growth [7,8]. Many efforts have been devoted to developing various seed layers for the 2D growth of Ag thin films, such as oxide, metal, self-assembled monolayers (SAMs), and polymer seed layers [9–15]. Alternatively, metal additives to Ag to form alloy is intriguing for improving metal wetting, which might benefit the seed-layer-free growth of ultra-thin Ag films [16–18]. Guo et al. demonstrated that the Al additive to Ag achieved a low percolation threshold thickness of 6 nm [1,19]. The 6 nm Al-doped Ag ultra-thin films exhibited a high transmittance of over 80% at 550 nm and an excellent thermal stability throughout the treatment of 300 °C in air. In contrast, the sheet resistance of the Al-doped Ag ultra-thin films, 70 Ω sq^{-1}, was inferior to those grown on seed layers due to a high residual resistivity from Al induced impurities and defects scattering according to Matthiessen's rule (i.e., 19.5 nΩ m/at% for Al) [20]. Instead of Al, Cu has a subtle residual resistivity (i.e., 0.68 nΩ·m/at%), which is promising for additives to Ag. Kim et al. [21] doped 10 wt% Cu to Ag thin films, achieving a satisfactory sheet resistance of 5.54 Ω sq^{-1}, but the optical transmittance was only 53.62% at 550 nm. Though the understanding on the Matthiessen's rule and the Ag-Cu alloy phase diagram [22] provides more insight into the additives to Ag, the growth kinetics, composition, and morphology of the ultra-thin Ag alloy films need to be further studied, especially, in the case of a small amount of doping.

In this paper, we report the magnetron sputtering deposition of the ultra-smooth and ultra-thin Ag thin films through doping a certain amount of Cu into Ag. The optical, electrical properties and stability of the thin films were studied systematically. The applications of these

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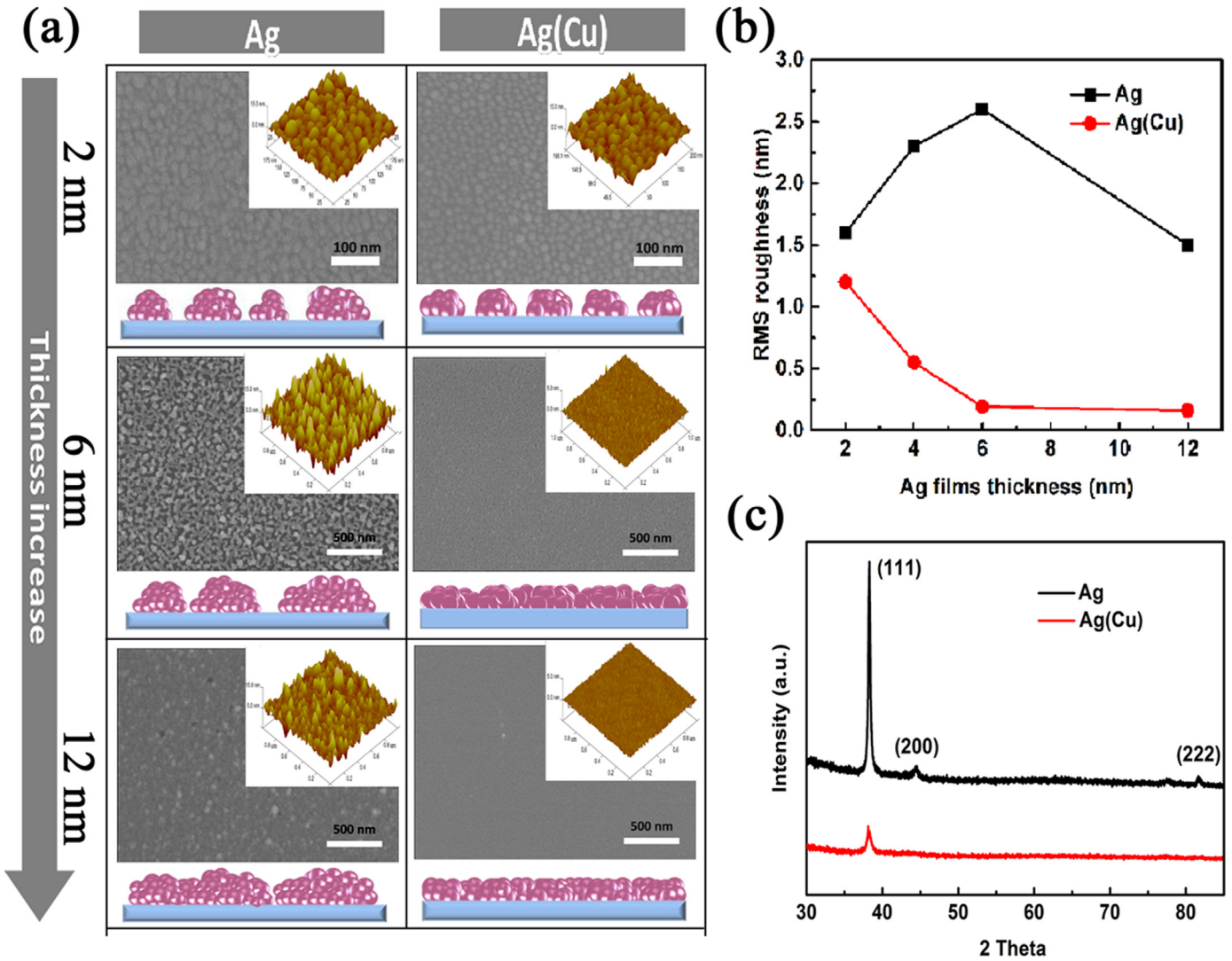

Fig. 1. (a) SEM micrographs of pure Ag thin films and Ag(Cu) thin films on glass substrates with increasing thickness. Inserts are the corresponding AFM images. Conceptual diagrams representing the evolution of pure Ag and Ag(Cu) clusters with increasing thickness. (b) RMS roughness of pure Ag thin films and Ag(Cu) thin films on glass substrates with increasing thickness. (c) XRD patterns of 50 nm pure Ag thin films and Ag(Cu) thin films.

thin films were also demonstrated using polymer solar cells as the model system.

2. Experimental details

2.1. Thin films preparation

Cu-doped Ag thin films were prepared using co-sputtering the 3 in. Ag and Cu targets on soda-lime float glass substrates (1 mm thick). Flexible PET substrates (with 10 nm SiO_2 over-layer) were used for mechanical flexibility measurements and preparation of polymer solar cell devices. The substrates were sonicated stepwise in acetone, ethanol and deionized water for 10 min each, and then dried with nitrogen. The sputtering chamber was evacuated to a base pressure of 5×10^{-4} Pa. High purity (99.999%) Ar (40 sccm) was introduced into the chamber with a pressure maintained at 0.7 Pa during sputtering. The sputtering power was fixed at 40 W for Ag and tailored in the range of 2–12 W for Cu deposition, respectively.

2.2. Fabrication of inversed polymer solar cells

The as-deposited PET/Ag(Cu) (8 nm, 10 Ω sq^{-1}) electrodes were applied for fabricating inversed polymer solar cells (I-PSCs) devices. For comparison, the precleaned PET/ITO (150 nm, 30 Ω sq^{-1}) electrodes (Zhuhai Kaivo Optoelectronic Technology Co.) were used as the control samples. A 20 nm ZnO layer was spin-coated onto the substrates from ZnO solution at 2000 rpm for 60 s [23]. Then the active layer with the different thickness was deposited by spin-coating from a PTB7-Th:$PC_{71}BM$ (1:1.5 wt%, 25 mg ml^{-1}) solution in the mixed solvents of CB:DIO (97:3 vol%) at 2000 (or 4000) rpm for 120 s. Photoactive materials PTB7-Th and $PC_{71}BM$ were purchased from 1-Material Chemscitech Inc. (Canada) and American Dye Source Inc., respectively. Finally, a 10 nm MoO_3 and 100 nm Al as the anode were deposited by thermal evaporation under vacuum at a pressure lower than 3×10^{-6} mbar. The effective device area was defined to be about 0.06 cm^2 by using a shadow mask. Details of the cell fabrication could be found elsewhere [23].

2.3. Characterization and measurements

The surface morphologies were observed using a field emission scanning electron microscope (FE-SEM, Hitachi S-4800) and an atomic force microscope (Veeco, Dimension 3100V). The optical transmission spectra were obtained at room temperature using a UV–Vis–NIR