



Improvement of MoO₃/Ag/MoO₃ multilayer transparent electrodes for organic solar cells by using UV–ozone treated MoO₃ layer

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ABSTRACT

Ultraviolet ozone (UVO) treatment of molybdenum trioxide (MoO₃) appears to be a simple and efficient method for obtaining highly continuous and smooth silver (Ag) thin films in the thermally evaporated MoO₃/Ag/MoO₃ (MAM) multilayered structure as transparent electrodes for small-molecule organic solar cells (OSCs). It is observed that UVO treatment can oxidatively modify the non-stoichiometric MoO₃ (or MoO_{3-x}) surfaces, further increasing the Mo⁶⁺/Mo⁵⁺ composition ratio and work function of MoO_{3-x}. Importantly, the use of UVO treatment for the MoO₃ bottom layer effectively improves the wettability of Ag on MoO₃ and enhances the lateral growth of Ag thin film, resulting in a reduction of the percolation threshold thickness of the continuous Ag layer. Due to the formation of an ultrathin Ag interlayer with a continuous and smooth surface morphology, the MAM multilayered electrode after UVO treatment of MoO₃ for 3 min has excellent optical and electrical properties, including a high maximum transmittance of 89.1% and a low sheet resistance of 8.0 Ω/sq. When the optimal UVO-treated MoO₃/Ag (7.5 nm)/MoO₃ films are used as the anode in OSCs with the copper phthalocyanine (CuPc)/fullerene (C₆₀) planar heterojunction structure, the OSCs have a power conversion efficiency of 0.55%, which is 2.0 and 1.2 times higher than that of devices with untreated MoO₃/Ag (7.5 nm)/MoO₃ (0.27%) and MoO₃/Ag (10 nm)/MoO₃ electrodes (0.46%), respectively, and competitive with that of indium-tin-oxide-based devices. Because of almost full surface coverage of the Ag interlayer, UVO treatment of MoO₃ in MAM multilayered electrodes can improve charge carrier injection/extraction at the anode contact and hence improve the photovoltaic performance of OSCs.

1. Introduction

Organic solar cells (OSCs) have unique properties, including light weight, low cost, simple processing, mechanical flexibility, and potential roll-to-roll mass production, making them very attractive as renewable energy devices [1,2]. They have been rapidly developed with advancements in materials, device architectures, and device processing [3,4]. A highly transparent and conductive electrode is of great importance for OSCs and other optoelectronic thin-film devices, as it greatly determines their efficiency. Currently, indium-tin-oxide (ITO) is the most commonly used material for transparent electrodes in OSCs owing to its excellent optical transparency and electrical conductivity [5,6]. However, the price of ITO has recently increased due to the limited reserves of indium, increasing the cost of devices based on ITO electrodes [7]. For top-illuminated OSC or top-emitting organic light-emitting diode applications, the sputter deposition process of ITO can damage the underlying organic layers, degrading device performance [8]. Furthermore, the brittleness and high-temperature processing of

ITO limits its utility for flexible optoelectronic devices. Therefore, considerable effort has been devoted to developing alternative materials for transparent electrodes, including transparent conducting oxides, carbon nanotubes, graphene, conducting polymers, metal nanowires or meshes, and patterned metal grids [9–12]. However, many of these alternative materials have either large sheet resistance or high surface roughness, which reduce short-circuit current density (J_{sc}), fill factor (FF), and power conversion efficiency (PCE) of OSC devices [10–12]. Therefore, novel transparent electrodes with good optoelectrical properties, mechanical flexibility, low cost, and low-temperature processing are desirable.

Recently, dielectric-metal-dielectric (DMD) multilayered electrodes have received interest as transparent electrodes due to their good optical and electrical properties and simple thermal evaporation process [13–15]. Moreover, with their intrinsic flexibility and high conductivity [16], DMD multilayered electrodes are suitable for roll-to-roll production with flexible substrates. Metals, such as Ag and Au, and various low-cost metal oxide materials, such as MoO₃, WO₃, TeO₂, and ZnO,

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have been evaluated as candidate materials for the DMD structure [13–16]. In particular, MoO₃ is one of the most promising materials owing to its non-toxic nature, easy thermal evaporation, and good energy level matching, which has been used as a buffer layer in OSCs and organic light-emitting diodes [17,18]. The evaporated MoO₃ film contains oxygen vacancies under an ultrahigh vacuum and has an n-type semiconductor property with a large electron affinity and ionization potential [19,20], suggesting that the hole injection/extraction process can be effectively achieved via electron extraction from the organic semiconductors adjacent to MoO₃. The electrical properties of DMD electrodes mainly depend on the metal layer. The transmittance of DMD electrodes can be enhanced by introducing two dielectric layers with high refractive indexes at the two sides of the metal layer, respectively. It should be noted that making the metal layer as thin as possible, while maintaining a smooth and continuous morphology, is of vital importance to obtaining good optical and electrical properties for DMD electrodes. In DMD systems, metal thin films grown on a dielectric material via thermal evaporation tend to form isolated islands during the deposition of the first few nanometers, leading to a non-conductive layer [21]. After further deposition, the percolation threshold, which is defined as an equivalent thickness at which separate metal islands start to connect and form a continuous and conductive layer, is reached and conductivity increases rapidly. Once the thickness of the metal films increases beyond the percolation threshold, the reflection of a typical continuous metal film increases toward the infrared regime, leading to a gradual decrease in the film transmittance [22]. Thus, the best trade-off between increasing conductivity and decreasing transparency is using a thickness close to the percolation threshold. However, few studies have attempted to reduce the metal percolation threshold, which is the key motivation of the present study.

One way to approach this issue is to introduce a high-surface-energy seed layer on the substrate, such as that made of Au, Al, or Ca [23], creating preferred nucleation sites to enhance lateral Ag film growth. This method significantly improves the wetting property of the Ag layer on the substrate, decreasing the percolation threshold (i.e., lowering film thickness), and thus reducing the resistance and increasing the transparency of the electrodes. For optoelectronic device applications, however, such a seed layer is likely to deteriorate device efficiency due to refractive index differences between Ag and seed layers. The growth of Ag islands can also be reduced by derivatizing the substrate with a layer of molecules designed to enhance Ag nucleation via strong interactions with both the substrate and the incoming Ag atoms [24]. However, this method cannot be applied for large-scale production because of the long reaction time and complicated synthetic procedure. Ultrathin continuous Ag films are produced at low temperatures and high evaporation rates [21,25]. Reducing substrate temperature and increasing evaporation rates generally reduce the surface diffusion of Ag atoms, and thus alter the standard nucleation process. Although a low-temperature process may be useful for the growth of ultrathin Ag layers, the process cost is high due to the requirement of equipment needed to maintain a low temperature.

Ultraviolet-ozone (UVO) treatment technique is widely used in most optoelectronic devices for cleaning and modification purposes by using the photo-sensitized oxidation process. UVO treatment has been shown to effectively remove organic contaminants, such as hydrocarbons from surfaces, as well as create a more hydrophilic surface, and is often utilized to increase the work function of electrodes or buffer layers [26–29]. Applying UVO treatment to ITO is expected to improve OSC performance by increasing the hole-extraction efficiency [28]. Applying UVO treatment to a PEDOT:PSS buffer layer results in the formation of a metastable surface dipole [29], which leads to an enhancement in the work function, thus increasing hole extraction from the photoactive layer. Recently, Fang et al. treated an MoO₃ surface by UVO to reduce surface defects and to create better contact with the photoactive layer [30]. The present study uses UVO treatment to photo-chemically modify the surface of the MoO₃ bottom layer in MoO₃/Ag/MoO₃

(MAM) multilayer transparent electrodes, and investigates its effects on the surface properties of MoO₃ films, surface morphology of MoO₃/Ag films, optical and electrical characteristics of MAM electrodes, and photovoltaic properties of OSCs with MAM electrodes. Moreover, the dynamics of charge injection, extraction, and accumulation at the electrode/organic interface in OSCs are studied experimentally using capacitance-voltage (C-V) and impedance spectroscopy (IS) measurements.

2. Experimental

2.1. MoO₃/Ag/MoO₃ electrode deposition and characterization

Prior to MAM electrode deposition, glass substrates were scrubbed in a detergent solution (Merck Extran). They were then immersed sequentially in a heated ultrasonic bath of de-ionized (DI) water, isopropyl alcohol, and ethanol for 15 min each, followed by a rinse in DI water. Finally, the substrates were blown dry with nitrogen gas prior to use. The MAM multilayered electrodes were deposited sequentially at room temperature on the cleaned glass substrates via thermal evaporation under high-vacuum ($\sim 5 \times 10^{-6}$ Torr) conditions. The evaporation rates of MoO₃ powder (99.9995%, Alfa Aesar) and Ag shot (99.999%, Summit-Tech) were kept at 0.4 and 1.0 Å/s, respectively. The thickness of the Ag film was varied from 4.5 to 13 nm, while that of the bottom and top MoO₃ films was fixed at 20 nm. The deposition rates and the film thicknesses were measured in situ using a quartz crystal microbalance (Sycon Instrument, STM-2XM), and the latter was further calibrated ex situ using a surface profilometer (Tencor, Alpha-step IQ). Thickness measurements by profilometer were made at five locations on the sample surface, including four angularly symmetric spots at the edge and one spot in the center. The thickness variation is about 2% for Ag layer and 5% for MoO₃ layer, respectively over ~ 10 mm spot distance. The good uniformity of the film thickness can be attributed to the design of the rotating sample holder and proper evaporation distance between evaporation source and substrate during the vacuum deposition process. For the fabrication of UVO-treated MAM multilayered electrodes, the glass/MoO₃ samples were taken out of the vacuum chamber after the deposition of the MoO₃ bottom layer, and then irradiated in a home-made UVO treating apparatus. The UVO treating apparatus is a stainless-steel cell (150 × 300 × 100 mm³) with a high-intensity and low-pressure mercury vapor lamp affixed to its roof and controlled by a timer to regulate irradiation. The lamp emits UV light (power density = ~ 335 W/m²), principally at 184.9 and 253.7 nm wavelengths which excite molecular oxygen to form ozone. After warming the UV lamp for 20 min, the glass/MoO₃ samples were placed on a sample stage 2 cm from the UV lamp and then treated for irradiation times within the range of 0–5 min under atmospheric conditions. Subsequently, the UVO-treated glass/MoO₃ samples were placed back into the vacuum chamber to complete the fabrication of the MoO₃/Ag/MoO₃ multilayered structure.

The surface electronic structure and variation in the work function of MoO₃ films were determined using a photoelectron spectrometer (VG Scientific Sigma probe) with a monochromatic aluminum K α source (1486.6 eV) for X-ray photoelectron spectroscopy (XPS) measurement and a photoelectron spectrometer (Riken Keiki, AC2) for UV photoelectron spectroscopy (UPS) measurement, respectively. The contact angle of MoO₃ thin films was measured using the Sessile drop technique under ambient conditions. DI water (H₂O) and methylene iodide (CH₂I₂) were used as test liquids. The surface morphology of MoO₃ and MoO₃/Ag films was characterized using scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. The SEM and AFM images were taken by a field-emission scanning electron microscope (Hitachi, SU8000) and an atomic force microscope (Veeco Instrument, Dimension 3100) in tapping mode, respectively. The spectral transmission and reflectance were recorded using an ultraviolet-visible (UV-vis) spectrophotometer (Thermo, Evolution-300)

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