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Observation of feature ripening inversion effect at the percolation threshold for the growth of thin silver films

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ABSTRACT

The growth behavior of thin silver films on organic layers is investigated during deposition by means of simultaneous in-situ monitoring of sheet resistance and transmittance. Thermally evaporated films up to 11 nm show a distinct percolation behavior with strong resistance drop at the percolation thickness. Additionally, evaporations are divided into a sequence of one nanometer steps. In the deposition breaks, the films exhibit a ripening effect with an inversion at the percolation thickness, by changing from an increasing to decreasing sheet resistance over time. Scanning electron micrographs suggest same ripening mechanisms for islands below the percolation thickness as for holes above.

1. Introduction

Recently, increasing efficiencies of organic solar cells show the potential of this technology to supply the world with renewable on-site solar energy [1]. One obstacle towards this goal is the brittleness of standard metal oxide transparent electrodes impeding industrial production on flexible substrates with roll to roll processing lines [2]. Among other techniques, a very promising alternative is the usage of ultra-thin metal electrodes which can be deposited in low-energy evaporation processes as bottom and top contacts. In dielectric–metal–dielectric systems, they provide high optical transmission and extremely low sheet resistance while maintaining flexibility [3,4].

In this work thin silver films have been investigated as transparent electrodes for utilization in organic devices. Preparation was carried out via thermal evaporation in vacuum chambers. The silver films were deposited on doped organic hole transport layers acting as mimicking layers for a complete device. Thus the growth behavior on an actual device was preserved while keeping the whole sample transparent and simple. Sheet resistance and transmittance of the silver films were measured in-situ during the deposition and scanning electron micrographs were taken afterwards. With such experiments the growth of thin silver films could be monitored and analyzed.

Metals like silver tend to agglomerate during thermal evaporation on most substrates. Because of this Volmer–Weber growth behavior, islands form within the first few nanometers of deposition [5,6]. These islands act as nanoparticles and show plasmonic effects. Localized surface plasmons are excited with their excitation energies being proportional to the island's diameter [7,8]. These effects cause scattering and absorption, strongly diminishing the film transmittance. With further deposition, the silver islands grow until they are only separated by narrow trenches down to the substrate. Now paths of electrical conductance form over the whole sample due to island coalescence, defining the point of percolation (POP). At the same point, localized surface plasmon excitation is strongly suppressed. A trade-off between transmittance and sheet resistance is observed with ongoing deposition. This growth behavior can be strongly influenced by the use of different electrode metals, substrates, temperatures, deposition rates, and surfactants [6,9–11].

To gain insight to ripening processes, silver deposition was interrupted after every nanometer. Thereby in-situ measurements could be compared to ex-situ measurements and scanning electron microscope (SEM) pictures. During the evaporation breaks, the sheet resistance showed significant change, indicating a ripening of the film. A feature ripening inversion could be observed around the POP.

2. Experimental details

Material evaporation took place in a high vacuum chamber (CreaPhys GMBH, Dresden, Germany), which is connected to a *glovebox* (MBraun, Garching, Germany) with nitrogen atmosphere. This enables sample preparation under inert conditions with a residual amount of water and oxygen below 1 ppm. Evaporation processes were carried out at around 1×10^{-4} Pa. On 2.5 × 2.5 cm^2 BK7 glass substrates (Schott, Mainz, Germany) an organic hole transport layer consisting of 20 nm of N,N′-((diphenyl-N,N′-bis)9,9,-dimethyl-fluoren-2-yl)-benzidine (BF-DPB) doped with 10 wt.% of 2,2-(perfluoronaphthalene-2,6-diylidene) dimalononitrile was deposited by thermal evaporation from Al_2O_3

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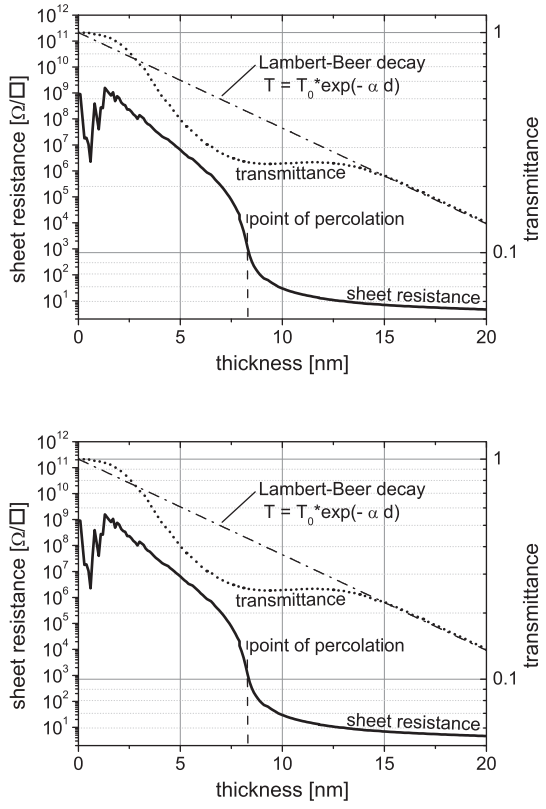

Fig. 1. Sheet resistance and transmittance of a silver film on 20 nm of p-doped BF-DPB vs. thickness *d* for a standard in-situ monitor evaporation. The point of percolation (POP) is marked with a vertical line. Here silver islands connect to conductive grid.

crucibles, which were heated electrically. Silver films where then deposited from molybdenum evaporation boats, also heated by an electric current. The electrical and optical performance of the electrodes was measured during evaporation of the silver layer with the in-situ monitor — a custom-made measurement tool which enables in-situ measurements of a four-point probe sheet resistance, transmittance and sample temperature using a Keithley 2400 source measuring unit (Keithley Instruments, Ohio, USA), two SFH206K photodiodes (OSRAM, München, Germany) (transmittance and reference) for an integrated transmittance and an Alumel®–Chromel® thermocouple. The Keithley 2400 is connected to two pre-evaporated aluminum contact pads of 50 nm thickness, defining an electrode measurement area of 78.2 mm^2. Film thickness was logged during the measurement using a calibrated quartz microbalance. In case of layer thicknesses below 10 nm, the films are neither smooth nor closed. There the given thickness should be regarded as nominal, indicating the amount of material on the sample. For ripening investigations, 11 nm of silver was evaporated in 1 nm steps with two minute breaks between successive evaporations. Scanning electron micrographs were taken with a Zeiss ΣIGMA field emission scanning electron microscope (Zeiss, Oberkochen, Germany) with electron beam acceleration voltages at 20 kV.

3. Results and discussion

Before analyzing the ripening processes in the silver electrode microstructure, first a continuous, uninterrupted silver deposition is investigated to understand the fundamental processes in the metal electrode growth. Fig. 1 shows sheet resistance and transmittance data versus layer thickness of a continuous silver evaporation on an organic layer described above. The growth process of such layers can be divided into three regimes. First, the island regime with a slow decline in sheet resistance, then a sudden decrease around the POP at roughly 8 nm, and finally a bulk-like region in which the conductivity of the layer increases very slowly. The initial decline in sheet resistance in the island regime until 6 nm is caused by growing islands of highly conductive silver and narrowing paths between them. Island growth continues until coalescence sets in around the POP. As the SEM images in Fig. 2 show, some islands have already started interconnecting at 6.5 nm, below the POP, but there is no long range connection detectable. Around the POP, there is a rapid decline of the sheet resistance because of fast island coalescence across the entire sample. At this critical layer thickness of 8 nm, a conductive network is built. At 9 nm, after the POP most of the islands are interconnected, see Fig. 2, and the sheet resistance enters the bulk regime. Further deposition does not drastically alter the film microstructure. These regimes match the transmittance curve very well. It nicely follows the Lambert–Beer exponential decay for large thicknesses in the bulk regime above 13 nm thickness. For thinner films from 3 to 13 nm, the transmittance falls below the Lambert–Beer trend, with the highest deviation around the point of percolation. In this region, plasmonic absorption is observed due to localized surface plasmons in silver islands acting as nanoparticles. Once the islands interconnect, localized surface plasmons can no longer be excited and the transmittance follows the Lambert–Beer behavior. The turning point of the transmittance curve coincides well with the POP.

To compare in-situ with ex-situ measurements, non-continuous depositions were performed which show an inversion of the feature ripening at the POP. In Fig. 3 the experiment is repeated with evaporation breaks of 2 min after each nanometer. As expected from continuous evaporations, the sheet resistance falls during every deposition with a very strong decrease during the deposition of the 8th nanometer. We interpret this as the POP, which coincides very well in thickness with the previous measurements. Ripening processes can be seen in the breaks between depositions. Up to the deposition of the 7th nanometer of silver, increases in the sheet resistance are observed in the breaks afterwards. From the 8th nanometer on, there is a change in ripening behavior during the breaks. Decreases in sheet resistance can be seen afterwards in the subsequent deposition breaks.

The transmittance stays constant during the deposition breaks, indicating that the number of islands in total does not change before the POP. Otherwise additional or less plasmon excitations would alter the transmittance.

This suggests the following ripening behavior: Solitary silver islands have been reported to grow in a Volmer–Weber growth mode [12]. When no deposition is taking place, these islands contract and become more circular over time due to surface energy minimization to occupy as little space on the organic layer as possible. The low-conductivity gaps between islands thus widen during the deposition breaks and the sheet resistance rises. After the POP, most of the sample is interconnected and decreases in sheet resistance can be observed in evaporation breaks. However, this behavior is less pronounced the thicker the silver film becomes, suggesting holes in the silver film as ripening motor. Just as the islands before, the holes contract and thereby minimize their impact on the sheet resistance of the silver film. With higher film thickness, hole contraction becomes an increasingly negligible factor, but directly above the percolation thickness, island interconnections are thin and easily influenceable by hole reshaping.

These observations are in good agreement with literature. On organic sublayers, as used here, silver tends to form clusters [9]. At room temperature silver clusters of several atoms have often been reported to move bodily across highly oriented pyrolytic graphite, a fast diffusion process in which a cluster moves as one entity without changing its shape [13–15]. We expect similar bodily diffusion in our experiments, until a critical island nucleation size is exceeded by merging of several clusters. Afterwards the islands cannot move as an entire entity anymore, but island reshaping can occur driven by system energy minimization [16]. A reshaping of bigger silver islands at temperatures above 100 °C has been shown in annealing processes [16,17]. This is likely to happen in our system, as studies show strongly increased mobility towards thinner

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