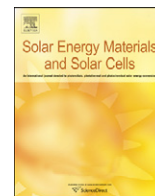




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Fabrication and characterization of large metallic nanodots arrays for organic thin film solar cells using anodic aluminum oxide templates

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ABSTRACT

We present a soft method for the fabrication of well controlled plasmonic nanodots on large ITO substrate for organic solar cells. Masks of nanopatterned aluminum oxide are elaborated and deposited on ITO substrates before metal deposition. After removal of the mask, well organized and isolated metallic nanodots are observed. In this article, we focus on gold or silver nanostructures: they show a Surface Plasmon Resonance (SPR) in the visible region, an important feature for their integration in organic thin film solar cells and the final improvement of the optical properties of the cell. In addition, their near field enhancement capacity is also clearly demonstrated by surface enhanced Raman spectroscopy and FDTD method simulation. An additional advantage of this protocol is that it can be used on any kind of surface and with different metals, depending on the final application.

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1. Introduction

One extremely promising way for the further development of solar cells is based on the use of nanomaterials: silicon nanowires [1], nanostructuring of active materials [2]. Among all those structures, the use of plasmonic metallic nanostructures has led to many studies [3]. Such nanostructures act as nanoantennas [4] to trap the light. As a consequence, they are extremely interesting for thin film solar cells, the absorption of those cells being generally rather poor. The plasmonic absorption and optical properties [5] of metallic nanoparticles can be used to enhance the optical absorption of the global cell. The role of those plasmonic nanostructures in the final optical properties of the cell is based on two features: the strong electromagnetic near field enhancement and the large scattering cross-section of plasmons at the resonance wavelength, the exact relative contribution of those two features remaining unclear.

As a consequence, metallic nanostructures are used successfully for silicon solar cells [6] and organic solar cells [7]. Their role in the

final electrical properties of the cell is also studied [8]: shunt current and change of the work functions of the electrodes can occur after integration of metallic nanostructures. In the case of hydrogenated amorphous silicon solar cells, Kim et al. [9] have shown that the use of metallic nanostructures (with high work function) is beneficial for the electrical properties of the cell. Nevertheless light trapping in such a cell strongly depends on the plasmonic nanostructures themselves: it can strongly vary with their size, the surrounding material, their shape, the nature of the metal and their organization [10–13]. The precise control of all those parameters is essential to optimize the final optical properties of the cell. In addition, the preparation protocol of those nanostructures should be easily performed on the large surface used in solar cells. In the case of organic cells, the most common material used as anode is Indium Tin Oxide (ITO) which has to be considered as surface for structures deposition. To our knowledge, few techniques are developed to prepare and precisely control the above parameters for this kind of surface. Electron Beam Lithography (EBL) offers an extremely efficient method for the control of all those parameters. This method is extensively used for the preparation of Surface Enhanced Raman Spectroscopy (SERS) substrates [14–17], this measurement technique being based on the large near field enhancement associated to those nanostructures

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[18]. Nevertheless, this method is extremely expensive, time consuming and cannot be used for the preparation of very large samples. In this article, we propose an alternative, inexpensive and reproducible method, based on Anodic Aluminum Oxide (AAO) lithography. This technique allows elaborating onto any plane substrate highly uniform and periodic arrays of metallic nanodots with hexagonal configuration. In the particular case of gold or silver, surface plasmon resonance frequencies are situated in the visible spectrum, a key parameter for organic photovoltaic applications. Metallic nanodots fabrication with AAO lithography is already shown on silicon [19] and for GaAs solar cell application [20] but to our knowledge this technique is never used for ITO substrates dedicated to organic photovoltaic cells (OPV). As ITO is extremely sensitive to chemical treatment [21], few methods can be used for the fabrication of organized metallic nanostructures on large surface. Therefore in this work, gold and silver nanodots are prepared on a glass/ITO substrates using AAO lithography. This technique, extremely efficient for the preparation of nanostructures [22,23], is here carefully adapted to ITO substrate: AAO masks prepared with our protocol are also optimized for metallic thermal evaporation and are thinner (around 400 nm) than commercial [24] and traditional AAO membranes described in literature [22,25]. The final optical properties of those samples are carefully studied by optical transmission measurement associated to FDTD method calculations. In addition, the optical near field efficiency of such nanostructures is checked by SERS measurements. The final samples clearly show extremely promising optical properties for their integration in organic solar cells.

2. Materials and methods

In this work, we use a nanoporous AAO template to deposit metal through the mask and obtain controlled plasmonic nanostructures after AAO mask removal. Highly ordered AAO nanopore arrays are fabricated by a two-step anodization process [22,25]. Commercial high purity aluminum wafers (diameter 3 cm, purity 99.999%) are electro-polished (20 V) for 10 min in a mixture of

perchloric acid HClO_4 and ethanol $\text{CH}_3\text{CH}_2\text{OH}$ (1:4) at room temperature under vigorous stirring. For the first anodization step, the pore spacing and pore diameters of the porous AAO can be controlled by electrolyte, anodic voltage and temperature. In this work, we focus on pore spacing of 100 nm and a pore diameter of 40 nm, applying the following parameters: a 0.3 M oxalic acid solution at 8 °C and a 40 V anodization voltage for 24 h.

Self-ordering of the pores takes place with increasing alumina thickness. This sacrificial alumina layer is selectively removed in a $\text{H}_2\text{CrO}_4/\text{H}_3\text{PO}_4$ mixture for 24 h at 45 °C leading to a nano-templated aluminum substrate. At this point, we can fix the AAO membrane thickness: it can vary from 100 nm to 100 μm as shown with the SEM images in Fig. 1f, depending on 2nd anodization time (Fig. 1a). The patterned aluminum substrate is then anodized for 5 min in the same experimental condition as for the 1st anodization, leading to a 400 nm thick alumina layer exhibiting a hexagonal lattice as shown in the inset of Fig. 1f. A key point is the thickness of the layer to avoid any shadow effect during metallic evaporation. In addition, lowering the thickness of the mask also drastically increases its flexibility, which, combined with the ozone treatment for hydrophilicity, enables the perfect sticking of the mask onto the ITO substrate and a subsequent coverage with metallic nanodots (typically cm^2) after metallization step.

The resulting AAO film is released from the aluminum sheet using a mixture of $\text{CuSO}_4:\text{HCl}:\text{H}_2\text{O}$ for 30–60 min. (Fig. 1b). The back ‘barrier layer’ of this thin AAO film is removed using chemical wet etching (Fig. 1c). At this point, the chemical wet etch process time affords to set the final size of bottom AAO pores from 45 nm to 80 nm (inset of Fig. 1f and Electronic supplementary information Fig. c), keeping the same distance between AAO pores (100 nm). We etch the back barrier layer in a 5 wt% phosphoric acid solution for typically 15–20 min at 35 °C to obtain AAO bottom pore size of 45–80 nm to leave a fully opened, free-standing AAO film (Fig. 1c), floating on top of water in the beaker. We can see in Electronic supplementary information Fig. a, an optical image of different free-standing nanoporous films floating on water. These templates are around 3 cm of diameter.

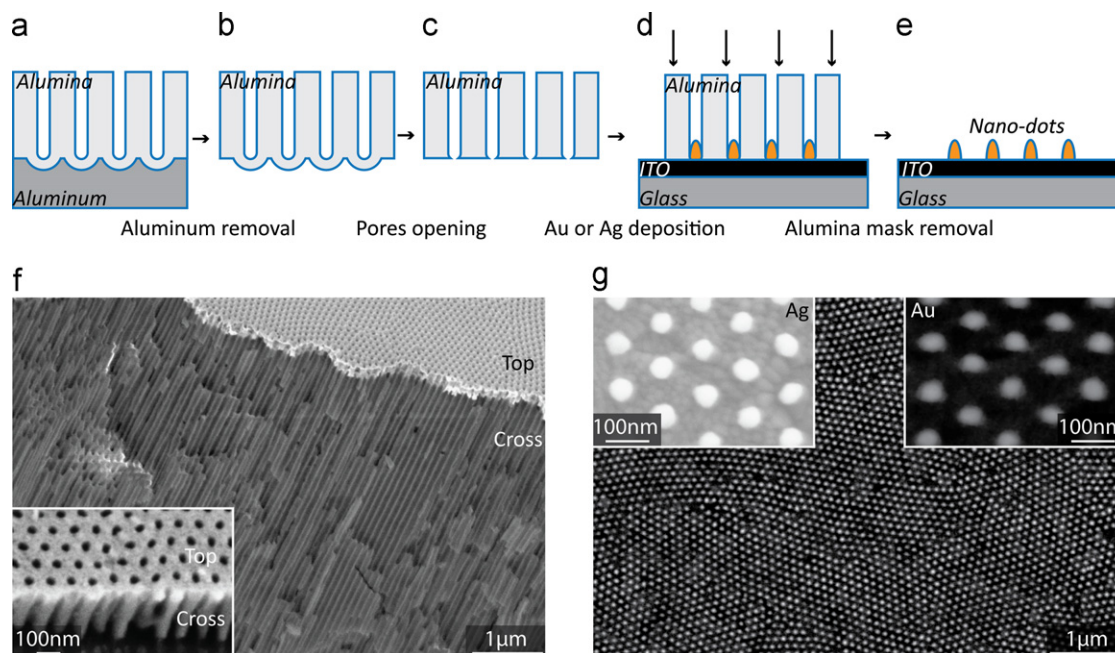


Fig. 1. (a)–(e): Metallic nanodots fabrication steps. (f): a typical SEM cross-section image of a thick AAO membrane and in the inset, a SEM cross-section image of a 400 nm AAO film on ITO surface (pore diameter: 45 nm). (g): SEM image of gold nanodots on ITO surface (diameter: 45 nm), Insets: a detail SEM image of silver (left) and gold (right) nanodots on ITO substrate.

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