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Nanostructured columnar heterostructures of TiO_2 and Cu_2O enabled by a thin-film self-assembly approach: Potential for photovoltaics

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ABSTRACT

Significant efforts are being devoted to the development of multifunctional thin-film heterostructures and nanostructured material architectures for components with novel applications of superconductivity, multiferroicity, solar photocatalysis and energy conversion. In particular, nanostructured assemblies with well-defined geometrical shapes have emerged as possible high efficiency and economically viable alternatives to planar photovoltaic thin-film architectures. By exploiting phase-separated self-assembly, here we present advances in a vertically oriented two-component system that offers potential for future development of nanostructured thin film solar cells. Through a single-step deposition by magnetron sputtering, we demonstrate growth of an epitaxial, composite film matrix formed as self-assembled, well ordered, phase segregated, and oriented nanopillars of *n-type* TiO_2 and *p-type* Cu_2O. The composite films were structurally characterized to atomic resolution by a variety of analytical tools, and evaluated for preliminary optical properties using absorption measurements. We find nearly atomically distinct TiO_2–Cu_2O interfaces (i.e., needed for possible active *p*–*n* junctions), and an absorption profile that captures a wide range of the solar spectrum extending from ultraviolet to visible wavelengths. This high-quality materials system could lead to photovoltaic devices that can be optimized for both incident light absorption and carrier collection.

1. Introduction

Recently, there has been great interest and progress in the development of controlled, vertically segregated thin film nanocomposites, particularly combinations of oxide systems that, due to the unique structures and interfacial properties, may provide new functionality for a variety of magnetic and electronic phenomena [1,2]. To date, there has been limited work on targeting self-assembled vertical oxide heterostructures for photovoltaic applications. Rather, in recent years the development of planar geometry, single junction thin film solar cells, in particular cadmium telluride (CdTe) and copper–indium–gallium–diselenide (CIGS), has aimed to provide solar energy conversion at lower cost than the established conventional silicon technologies. Presently, CIGS has demonstrated the highest lab-scale cell efficiency at 19.9% [3] with CdTe (16.5%) [4] close behind. However, broad viability is limited by issues associated with low-film qualities, complexity of the manufacturing processes, and scale-up yield. To surmount some of those difficulties and potentially realize higher efficiencies, new approaches such as multi-junction solar cells (with efficiencies of over 40%) [5], dye sensitized solar cells, bulk heterojunctions and organic cells have emerged [6–8]. However, these technologies presently exhibit high manufacturing costs or inadequate efficiencies, poor durability and poor photo-stability, precluding their commercial viability. One of the central issues for low conversion efficiencies in conventional planar *p*–*n* junction configurations (i.e., thin film multi-layer architectures) is the small minority carrier diffusion length for recombination due to inhomogeneous media, grain boundaries and structural defects (e.g., dislocations, vacancies). On the other hand, nearly one dimensional nanostructured materials including nanorods, nanowires, and nanotubes have been explored as components of photovoltaics (PV) to enable substantial light absorption due to their large surface area and enhanced light trapping capabilities [9–12]. As has been shown on fundamental grounds [13], these nanostructures also have the benefit of requiring only short minority carrier diffusion distances (thereby compensating for short minority carrier lifetimes) and provide efficient spatial carrier separation,

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potentially eliminating one of the key limitations of planar device architectures. In effect, a semiconductor device consisting of nanostructures arranged in vertically aligned arrays of radial *p*–*n* junctions can reduce the occurrence of recombination events and hence may relax the stringent requirements on material quality [9,14,15]. However, despite these attributes PV solar cells based on nanostructured assemblies have yielded poor conversion efficiencies (~0.5–6%) [9,11,16,17]. Possible causes of low efficiencies include non-optimized dimensions and composition, poor density/alignment/ordering of the nanostructures, and low quality heterojunction interfaces. To date, such structures have proven complicated to synthesize at the needed nanoscale, often relying on elaborate techniques that are unsuitably expensive for commercial production.

In this work we demonstrate self-assembled, highly ordered epitaxial nanostructured arrays of TiO_2:Cu_2O, having vertically-aligned interfaces that offer potential to overcome these limitations. Direct band-gap TiO_2 and Cu_2O have been extensively studied as PV materials and photocatalysts for solar energy utilization due to their excellent chemical stability, photostability, non-toxic nature, high abundance and low-cost [18,19], and recent advances were reported in the fabrication of polycrystalline granular or core-shell arrays that exhibited photovoltaic activity, albeit with low efficiency [20,21]. The band gap energies of *n*-type TiO_2 and *p*-type Cu_2O are about 3.2 and 2.1 eV, respectively; these band gaps enable photo-absorption from ultraviolet to the visible region. Furthermore, from a thermodynamic standpoint, the conduction band minimum and valence band maximum of TiO_2 lie below that of Cu_2O, satisfying a key requirement for efficient transfer of both electron and hole minority carriers [19]. Additionally, Cu_2O presents attractive characteristics for photovoltaic devices such as a high optical absorption coefficient and high minority carrier diffusion length as well as relatively good carrier mobility [22,23]. By selecting the TiO_2:Cu_2O system, this study exploits material self-assembly [1,2,24,25], since the component phases exhibit comparatively similar crystal structures [tetragonal-TiO_2 (anatase), cubic-Cu_2O], complete TiO_2–Cu_2O immiscibility, and a lattice parameter difference (~12% misfit) which is suitable for driving the self-assembly. The present method utilizes a simple single step fabrication methodology and demonstrates growth of these unique composite-nanostructured epitaxial-films. This approach could provide a path forward to create highly ordered nanostructured epitaxial film heterostructures with controlled microstructures and low defect concentration that promotes cost-effective fabrication of high efficiency, large-area photovoltaic devices.

2. Experimental details

The deposition of all oxide layers was conducted with an *rf*-magnetron sputtering system. Substrates were prepared by first depositing epitaxial TiO_2 buffer layers on (1 0 0)-surface $LaAlO_3$ (LAO) single crystals, followed by growth of composite TiO_2:Cu_2O films. The sputter targets were prepared from a single-phase anatase TiO_2 (for buffer growth) and a mixture (for composite film growth) of 50 mol% Cu_2O (99.9%, Alfa Aesar) and 50 mol% TiO_2 (99.9%, Alfa Aesar) powders, which were packed into 2 inch diameter copper trays. The sputtering system was initially pumped to a base pressure of 2×10^{-6} Torr and buffer/composite film depositions were carried out in ~5 mTorr argon atmosphere. Epitaxial growth of ~200 nm-thick composite films was established at substrate temperatures of 650 °C and 700 °C, respectively. Substrates were attached to the heater plate using conductive silver paste.

The crystalline quality and phase content of the samples were analyzed by a Philips Model XRG 3100 X-ray diffractometer. Crystallographic texture of the deposited layers were analyzed using a 4-circle X-ray diffractometer employing a Cu source operating at 50 kV and 100 mA and a bent graphite monochromator tuned to Cu K.

The X-ray photoelectron spectroscopy (XPS) examination was carried out to determine the oxidation states of Cu and Ti on and at the near surface of the film. A Thermo Scientific K-Alpha XPS instrument was used to collect data on both as-received as well lightly sputter etched sample surfaces. Monochromatic Al-K_α X-rays were used to collect core level spectra with an electron energy analyzer operating at a pass energy of 50 eV. Ar-ion sputter etching was performed at an ion energy of 3 kV with the sputter gun set at a calibrated etch rate of 15 nm/min on SiO_2 standard films.

Detailed cross sectional examinations of the composite films were conducted by conventional high-resolution transmission electron microscopy and Z-contrast scanning transmission electron microscopy (STEM). The Z-contrast images, with accompanying atomic-resolution electron energy loss spectroscopy (EELS), are sensitive to the atomic species through both the atomic number Z [26] and the EELS absorption edges. The STEM were recorded on a VG Microscopes HB603U fitted with an aberration corrector constructed by Nion Co. (Kirkland, WA), which offers a resolution better than 0.1 nm [27]. Conventional and high resolution TEM was also performed on a FEI CM200-FEG TEM/STEM instrument.

The optical absorbance measurements were performed in reflectance mode by a S.I. Photonics 400 CCD Array ultraviolet-visible (UV-vis) spectrometer. The analysis range was from 350 to 950 nm, and $BaSO_4$ was used as a reflectance standard. Room temperature Hall effect measurements were conducted on sputter deposited planar Cu_2O and TiO_2 films to establish *p*- and *n*-type carrier conductivities, respectively.

3. Results and discussion

Shown in Fig. 1 is a typical θ–2θ X-ray diffraction (XRD) pattern of a composite film having nominal TiO_2:Cu_2O concentration, co-deposited from a single sputter target composed of 50 mol% TiO_2 and 50 mol% Cu_2O on a TiO_2-buffered (1 0 0) $LaAlO_3$ (LAO) single crystal substrate. In this substrate architecture, one of the phases (TiO_2) was chosen as a seed layer to simulate future development towards a prototype solar cell module, where the composite matrix should be sandwiched between the two conjugate phases (e.g., one possible architecture for an active module is illustrated in Supplementary Fig. S1). Fig. 1 shows evidence for well-crystallized TiO_2 and Cu_2O phases. The presence of the strong (0 0 *l*) peak reflections of tetragonal anatase-phase TiO_2 and cubic Cu_2O, along with the absence of any additional peak reflections from either TiO_2 or Cu_2O, indicate phase purity and excellent crystallinity, with

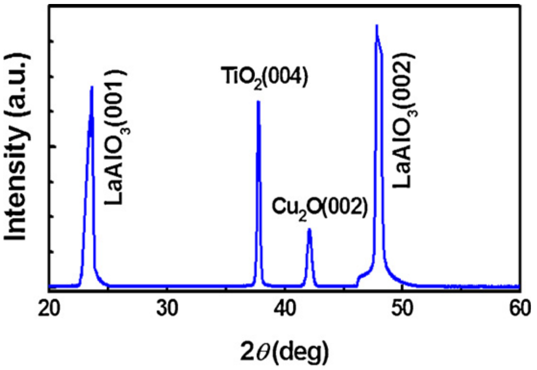

Fig. 1. The θ–2θ XRD scan of a mixed phase film with 50 mol% Cu_2O and 50 mol% TiO_2, deposited on TiO_2/$LaAlO_3$. The composite film exhibited preferred *c*-axis orientation. Peak heights of the $LaAlO_3$ reflections were truncated by detector saturation.