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Investigation of $LaVO_3$ based compounds as a photovoltaic absorber

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ABSTRACT

Bulk $LaVO_3$ (LVO) is known to provide an optical bandgap of 1.1 eV which is interesting for photovoltaic applications. Here, we compare the properties of LVO thin films using different techniques, namely pulsed laser deposition, spin coating by solgel and sputtering. ZnO/LVO p-n junctions were fabricated in order to obtain solar cell architectures. The grown films were analyzed with Surface photovoltage and Scanning Kelvin Probe Microscopy. The analysis of the junctions showed that the photogenerated electron-hole pairs are poorly separated and therefore not efficiently collected. LVO has shown the particularity to provide very high work function (4.6 eV) and a great dependence of the electrical and optical properties on the growth conditions, including the oxygen stoichiometry and the La/V ratio of the films.

1. Introduction

Inorganic thin film photovoltaics (PV) are mainly based on CdTe, amorphous Si or CIGS. In the most recent times, hybrid organo-metal halide perovskites have emerged with reported solar cell conversion efficiencies above 21%. However, these materials can present stability, reliability and toxicity issues (Petrović et al., 2015) but research has considerably progressed recently on these challenges. Alternative inorganic oxides could offer significant advantages regarding these issues while aiming at high conversion efficiencies. The ideal bandgap for a single bandgap active photovoltaic layer is around 1.3 eV for the solar spectrum on Earth. However oxides with such a low bandgap are scarce. To date, one of the most studied oxide as an active PV layer is cuprous oxide, Cu_2O. Its bandgap is around 2.1 eV which is not ideal for the solar spectrum. The conversion efficiencies are generally found to be around 4% (Ievskaya et al., 2015). Table 1 shows the most common oxide absorbers used to date in functional solar cells (SC). An emerging type of oxide SC is called ferroelectric photovoltaics (FE-PV), with recently improved conversion efficiencies of 3.98% for $BiFeO_3$ (Tiwari et al., 2015) and 8.1% with Bi_2FeCrO_6 (Nechache et al., 2015).

Oxide based SC, either based on *p-n* junctions or ferroelectricity, require the development of low bandgap oxides. One category of such oxides can be found among Mott insulators (MI). MI are materials that behave as insulators while they are predicted to be conductors under conventional band theories. However, MI can easily become conductive due for example to strain, defects, and oxygen stoichiometry. This phenomenon is called the Mott transition. Examples of MI are NiO, $LaVO_3$, $YTiO_3$, YVO_3, La_2CuO_4, Sm_2CuO_4, $LaMnO_3$ and $SrMnO_3$ (Nakamura et al., 2010; Arima et al., 1993).

In this work, we focus on the growth of $LaVO_3$ (LVO) thin films by different techniques and we investigate their optical and electrical properties for possible photovoltaic applications. The state of the art of MI based SC with an emphasis on LVO will be first presented. Then, we will show different fabrication routines for LVO thin film fabrication, giving rise to highly tunable properties such as conductivity and optical bandgap. Finally, we will describe the integration of LVO into SC and the limiting factors hindering the achievement of high efficiencies.

2. State of the art

Not all MI exhibit suitable bandgaps and properties for photovoltaics. The evolution of the optical gap has been studied in Arima et al., 1993. for $LaMeO_3$ and $YMeO_3$ compounds where Me is a trivalent 3d transition metal. Among the different materials, $YTiO_3$, YVO_3, $LaVO_3$, and $LaMnO_3$ present optical gaps close to 1.1 eV and can thus present an interest for PV applications.

MI – based SC are discussed theoretically in Manousakis, 2010. For narrow-gap MI, it is claimed that high quantum efficiencies of such SC

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Table 1
Examples of oxide absorber based SC, with their bandgap and solar cell efficiency.

Oxide absorber	Bandgap (eV)	Efficiency (%)	Reference
$BiMnO_3$	1.2	0.1	Chakrabartty et al. (2013)
CuO	1.2	0.08	Dimopoulos et al. (2013)
Bi_2FeCrO_6	1.4–2.1	8.1	Nechache et al. (2015)
Co_3O_4	1.5	0.02	Kupfer et al. (2015)
h-$LuMnO_3$/h-$YMnO_3$	1.5–1.55	0.11	Han et al. (2015)
Cu_2O	2.1	8.1	Minami et al. (2014, 2016)
$BiFeO_3$	2.2	3.98	Tiwari et al. (2015)
$(Pb_{0.97}La_{0.03})(Zr_{0.52}Ti_{0.48})O_3$	3.3	0.28	Qin et al. (2008)
$Pb(Zr_{0.53},Ti_{0.47})O_3$	3.4	0.22	Chen et al. (2012)
NiO	3.7	0.02	Warasawa et al. (2013)[a]

[a] Intentionally transparent to visible light SC.

can be obtained thanks to impact ionization and generation of multiple electron-hole pairs. Another theoretical study on MI SC but based on p-n junction mechanisms can be found in Charlebois et al., 2013.

There have been attempts to obtain MI based SC experimentally. For example, MI based heterojunctions (including La_2CuO_4, Sm_2CuO_4, $LaMnO_3$ and $SrMnO_3$) were studied by Nakamura et al. (2010). Very low photocurrents were obtained due to short minority-carrier diffusion lengths as compared to traditional semiconductors. The reason proposed for this is the strong electron correlation that enhances the effective carrier mass and lowers the electron mobility (Nakamura et al., 2010, 2007; Choi et al., 2010).

LVO is a p-type semiconductor in the bulk (Webb and Sayer, 1976; Madelung et al., 2000). Previous studies showed that LVO is orthorhombic at room temperature, with lattice parameters of a = 0.5555 nm, b = 0.5553 nm, and c = 0.7848 nm (Bordet et al., 1993). LVO films were grown by pulsed laser deposition (PLD) on different single crystal substrates (Masuno et al., 2004) and the oxygen partial pressure during growth was varied (Hotta et al., 2006). It was shown in Hotta et al., 2007 and He et al., 2012 that electronic reconstructions can occur at the $LaVO_3/SrTiO_3$ interface leading to conductive interfaces, similarly to the well-known $LaAlO_3/SrTiO_3$ case (Fix et al., 2009). However, the diffusion of oxygen vacancies in the $SrTiO_3$ substrate plays a role in the metallicity of the interface (Rotella et al., 2015). Following this idea of electronic reconstructions at the $LaVO_3/SrTiO_3$ interface, $SrTiO_3$ (0 0 1)//$(LaVO_3/LaFeO_3)_n$ heterostructures were proposed theoretically as SC, in which an internal potential gradient favours the separation of photogenerated electron-hole pairs (Assmann et al., 2013). In addition, experimental work on the fabrication of PLD grown LVO based solar cells is presented in Wang et al., 2015. Among the various LVO SC structures fabricated, only DSSC-type SC provided PV properties, however with low conversion efficiency (0.12%). This was attributed to trap-assisted recombinations and low minority carrier diffusion length (Wang et al., 2015), which is consistent with the interpretation of Nakamura et al. for similar MI materials (Nakamura et al., 2010, 2007).

To overcome these limitations, one possibility is to tune the carrier concentration of such materials. There are several possibilities to do this such as varying the La/V ratios and oxygen stoichiometry, and introducing additional substituents for La or V. Indeed, it was shown that V is present in 3+ and 4+ valence (Gharetape et al., 2011).

In the following, we will present our experimental procedure for growing LVO thin films as well as their structural, optical and electrical properties.

3. Experimental

Three LVO thin film fabrication techniques were used, namely pulsed laser deposition (PLD), spin coating by solgel and magnetron sputtering.

PLD was performed using a KrF laser with 10 Hz repetition rate and a fluence of around 2 J/cm^2 on the target. The target used was made of $LaVO_4$ prepared by solid state synthesis starting from La_2O_3 and V_2O_5 powders, milled, pressed and sintered at 700 °C for 10 h in air. The substrates used were $SrTiO_3$ (0 0 1) and 1 at.% Nb: $SrTiO_3$ (0 0 1) at a deposition temperature of 600 °C. The films were deposited and cooled down in either vacuum or in a $2.5 \cdot 10^{-5}$ mbar O_2 atmosphere.

Solution processed films were obtained as follows. First the required quantities of lanthanum (III) nitrate hexahydrate, vanadium (III) acetylacetonate, and barium nitrate (for Ba doping) were added into deionized water. Citric acid was dissolved in the solution together with ethylene glycol. A strong dark colored solution was obtained, excess of water was evaporated and a viscous liquid without precipitate appeared. This liquid was then spin coated on quartz substrates. The samples were heated at 400 °C with 1 h dwell in air, leading to the formation of a $LaVO_4$ film. Finally, post annealing was performed under H_2 at 900 °C with 1 h dwell to form the required $LaVO_3$ phase.

RF (Radio-Frequency) magnetron reactive sputtering of $LaVO_3$ was performed with an Orion 3 device from AJA International. Co-sputtered targets of La and V (Neyco) were used, with a power of 50 W and 100–130 W respectively. The substrates used were n-type (P) Fz Si (1 0 0) (0.8–2.5 Ω cm) and quartz substrates, heated at 400 °C. The Si substrates were cleaned before deposition using the "piranha" procedure and final HF dipping to remove the oxide at the surface. The Ar/O_2 gas flows were set to 8/2 sccm, with a deposition pressure of 3.4 mTorr. The substrate to target distance was kept constant at about 120 mm. Film thicknesses were in the 100–500 nm range. Post-deposition annealing was performed under H_2 at 900 °C with 1 h dwell to form the required $LaVO_3$ phase. For the formation of p-n junctions, ZnO was deposited as described in Soumahoro et al., 2011.

For PLD samples, X-ray diffraction (XRD) was performed in θ-2θ configuration with a Rigaku SmartLab X-ray diffractometer with a $CuK_{\alpha 1}$ beam of λ = 0.154056 nm. The same equipment was used for X-ray reflectometry (XRR) to determine the film thickness. For the sol-gel and sputtered samples, a Bruker D8 diffractometer with $CuK_{\alpha 1}$ beam was used.

The distribution and concentration of the chemical elements (La, V, and O) along the growth direction was obtained by Rutherford backscattering spectroscopy (RBS).

The optical properties were measured with a UV–vis-IR Perkin-Elmer Lambda 19 spectrophotometer, and an HORIBA Uvisel Lt M200 FGMS (210–880 nm) spectroscopic ellipsometer. The ellipsometric dispersion model used for $LaVO_3$ is based on the Tauc-Lorentz formula (Jellison and Modine, 1996). Hall effect was measured at room temperature to investigate the electrical properties of the thin films, using an Ecopia Hall effect system. I-V characteristics were performed at room temperature using an Oriel Solar Simulator in AM1.5G conditions and a Keithley 2450 SourceMeter.

Surface photovoltage (SPV) spectroscopy was performed using a short arc Xe lamp as a white light source, a SPEX 500M spectrometer, a chopper (300CD model by Scitec Instruments) as a reference frequency for the lock-in amplifier, used to evaluate the low SPV signal. A metal-insulator-semiconductor structure was used to extract the surface photovoltage signal. The set-up was realised by using an ITO (Indium Tin Oxide) coated glass slide as the transparent electrode and placing it in front of the sample to achieve the plate capacitor configuration, where the insulating spacer is simply air. Further details on the system can be found in Cavalcoli et al., 2015.

Atomic Force Microscopy (AFM) and Scanning Kelvin Probe Microscopy (SKPM) measurements were performed with a Park NX10 atomic force microscope at room temperature and ambient atmosphere.