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Interface atomic structure of LaCuOSe:Mg epitaxial thin film and MgO substrate

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ABSTRACT

In order to understand the growth mechanism of magnesium doped LaCuOSe thin film on MgO, the atomic structure of the interface between the epitaxial thin film and the substrate was investigated. Electron diffraction confirmed the orientation relationship between the film and the substrate as (0 0 1)[1 0 0]LaCuOSe:Mg//(0 0 1)[1 0 0]MgO. High resolution *Z*-contrast imaging based on the high angle annular dark field scanning transmission electron microscope (HAADF-STEM) technique clearly revealed the alternate stacking of La–O layers and Cu–Se layers, and identified a peculiar stacking sequence of La layers at the interface. With the aid of first principles calculations of the interfacial adhesive energy, it was found that the different La layers at the interface play a key role in stabilizing the interface.

1. Introduction

Compounds with the chemical formula LaCuOCh (Ch = S, Se) have attracted much attention due to their optical and electrical transport properties of wide band gap and p-type semiconductivity [1,2]. Optical and electrical properties have been investigated extensively with potential applications as transparent conducting materials, that is, hole injection electrodes for organic electroluminescence materials [3], or light emitting devices operating in the blue wavelength region [4]. Among these compounds, single crystal magnesium doped LaCuOSe films grown on MgO substrates by the reactive solid-phase epitaxy (R-SPE) technique [5,6] have been reported to show distinctive carrier transport properties [7–9]. High density hole doping of 1.7×10^{21} cm^{-3} was achieved on a 40 nm thick film, which is much larger than values obtained in the previously known wide-gap p-type semiconductors [7]. To obtain epitaxial thin films with such high hole concentration, it has been believed that the choice of the substrate crystal and involvement of a thin crystalline Cu layer as an epitaxy initiator is critical for the epitaxial growth in this system [10]. However, the growth mechanism of the epitaxial thin film of LaCuOSe on the MgO substrate has not been unraveled.

In this study, cross-sectional observations were made for a LaCuOSe:Mg epitaxial thin film deposited on a MgO substrate by the R-SPE method. The atomic structure at the interface between the epitaxial thin film and the substrate was investigated using a transmission electron microscope (TEM), a scanning TEM (STEM), and first principles calculations, with a special interest on the growth mechanism of the epitaxial thin film on the substrate.

2. Methods

2.1. Cross-sectional observation of the thin film

Magnesium doped LaCuOSe thin film was prepared by the R-SPE method [5–7]. In the method, a ceramic target with desired composition of LaCuOSe:Mg was ablated by a pulsed laser (KrF excimer laser) to deposit amorphous compound on a MgO(1 0 0) substrate. A thin crystalline Cu layer of 5 nm thickness was deposited as an epitaxy initiator before the deposition of the amorphous layer. Then, the deposited bi-layer film was sealed into an evacuated silica tube and annealed at 1000 °C to obtain epitaxially grown thin film. TEM samples for cross-sectional observation were prepared by a standard method employing mechanical grinding, dimpling, and Ar ion milling. Observations of TEM bright field images and electron diffraction were made using a conventional TEM (JEOL JEM-2010HC, 200 kV). High angle annular dark field (HAADF) STEM (HAADF-STEM) observations were performed using a STEM (JEOL JEM-2100F, 200 kV) equipped with the spherical aberration corrector (CEOS). The minimum probe size attained was about 1 Å.

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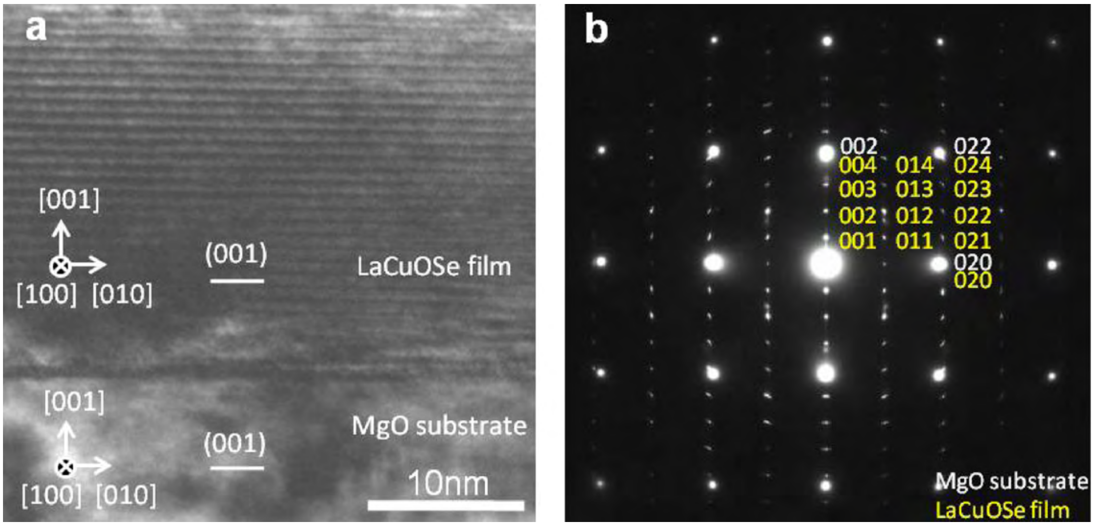

Fig. 1. (a) TEM bright field image and (b) selected-area diffraction pattern of the LaCuOSe:Mg/MgO epitaxial thin film.

2.2. Calculation of the adhesive energy

First principles total energy calculations of the compounds were performed to compute the adhesive energies of model film/substrate interfaces. Structure optimization and total energy calculations were made by a plane wave basis projector augmented wave (PAW) method [11] as implemented in the VASP code [12,13]. The exchange and correlation effects were treated by the generalized gradient approximation (GGA) [14]. The cutoff energy in the plane wave expansion was 400 eV. The optimized lattice constants of LaCuOSe and MgO were $a = b = 4.0746$ Å, $c = 8.8573$ Å and $a = b = c = 4.2554$ Å, respectively. Slab models of LaCuOSe and MgO were constructed by $1 \times 1 \times 3$ extension of the unit cell, which leads to slabs composed of 24 atoms for each compound. A vacuum layer of 15 Å was used for the slab calculations. To compensate for the lattice mismatch (4.2%), the lattice of LaCuOSe along the interface plane was expanded to fit to the MgO lattice. The resulting supercell with the size of 4.2554 Å × 4.2554 Å × 55 Å contains 48 atoms. The *k*-points were sampled according to the Monkhorst–Pack scheme [15] with a $4 \times 4 \times 1$ mesh. Atomic positions in the cells were relaxed until the residual forces became less than 0.05 eV/Å. Adhesive energies of the interfaces are obtained as the difference in energy between a sum of separated slabs of the film (LaCuOSe) and the substrate (MgO) and the attached slab with one interface. By our definition of the adhesive energy, a positive value of the energy corresponds to a stable and strong interface.

3. Results and discussions

Fig. 1 shows a bright field TEM image and the selected-area electron diffraction of the LaCuOSe:Mg/MgO epitaxial thin film grown by the R-SPE method. From the selected-area electron diffraction pattern, the orientation relationship between the film and the substrate was confirmed to be (0 0 1)[1 0 0]LaCuOSe:Mg//(0 0 1)[1 0 0]MgO. This orientation relationship is identical to that previously reported between a LaCuOS thin film and a MgO substrate [8].

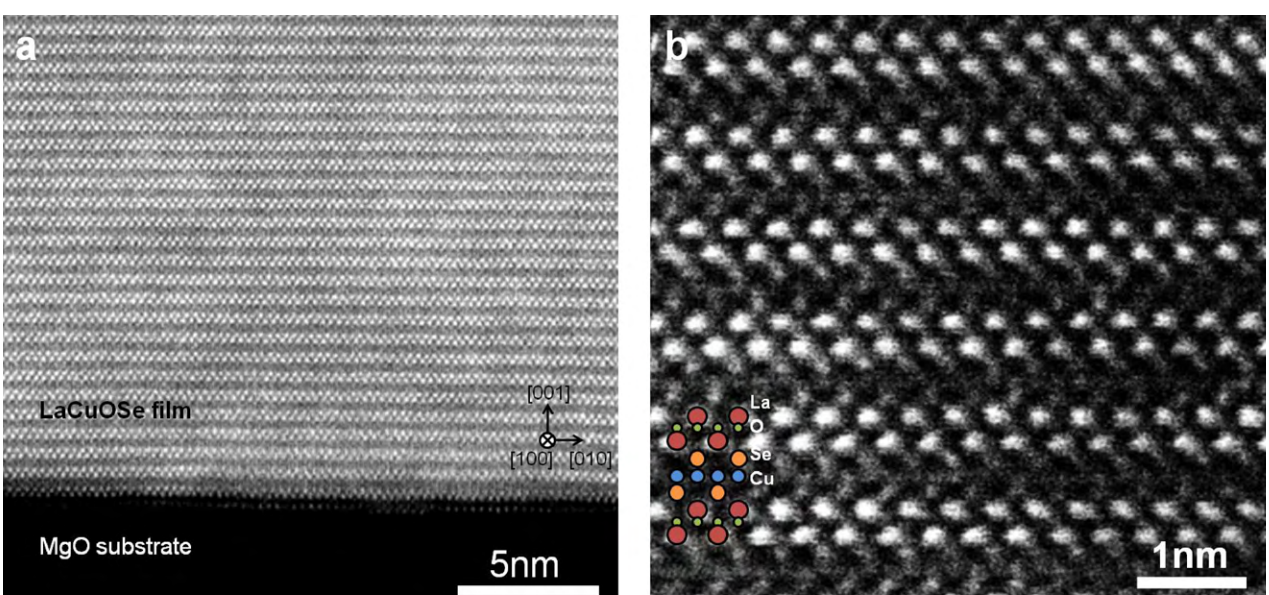

Fig. 2. (a) HAADF-STEM image of the LaCuOSe:Mg thin film deposited on the MgO substrate and (b) magnified image of the film, indicating that the La, Se and Cu columns are visualized. The atomic structure of LaCuOSe crystal is inset.