Observation of Microstructures in Doped La*M*O*X* Compounds by Atomic Scale STEM Imaging

Tetsuya Tohei[1], Teruyasu Mizoguchi[2], Hidenori Hiramatsu[3], Hideo Hosono[3], and Yuichi Ikuhara[1,4]

[1]Institute of Engineering Innovation, The University of Tokyo, Tokyo, 113-8656, Japan
[2]Institute of Industrial Science, The University of Tokyo, Tokyo, 153-8505, Japan
[3]Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, 226-8503, Japan
[4]Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan

Layered lanthanum oxychalcogenides with chemical formula of LaCuO*Ch* (*Ch* = S, Se) have attracted much attention due to their optic and electric transport properties of wide band gap and p-type semiconductivity. On thin film synthesis of the compounds, an epitaxial growth technique called reactive solid-phase epitaxy (R-SPE) method has been established in the last couple of years. Among these, epitaxial thin films of magnesium doped LaCuOSe grown on MgO substrate have been reported to show distinctive carrier transport properties; their electron transport depends on the thickness of the films, and high density hole doping of 1.7×10^{21} cm^{-3} was achieved on the 40 nm thick thin film [1]. However, detail of the film growth mechanism and the origin of such high-density hole doping has not been clear. In addition to this, recent discovery of superconductivity in fluorine doped LaFeAsO [2] has raised an interest on the crystal structure and the film growth of these isostructural compounds. The growth of 1111 type iron-arsenides superconducting thin films has been an important challenge because many technical difficulties still remain although the 1111 type has the highest critical temperature over 50 K among the Fe-based superconductor family [3]. In the present study, we have performed electron microscopic study of microstructures in the epitaxial thin films of doped LaCuOSe and LaFeAsO compounds. The scope of the present study contains two major interests: one is the observation of the film-substrate interface that may be responsible for the epitaxial growth mechanism, and the other is the investigation of lattice defects in the thin films that can be an origin of the significant transport properties in this system. In order to understand the growth mechanism of the LaCuOSe thin film on MgO substrate as well as the origin of the hole doping, atomic structure of the thin film was investigated using a transmission electron microscope (TEM) and a scanning TEM (STEM), in conjunction with first principles calculations. On the LaCuOSe:Mg/MgO epitaxial thin film, orientation relationship between the film and the substrate was confirmed as (001)[100]LaCuOSe:Mg//(001)[100]MgO from the selected area electron diffraction. Atomic scale observations of the thin film were made using a Cs-corrected STEM (JEM-2100F). From a STEM-HAADF (high angle annular dark field) and a BF (bright field) image of the LaCuOSe:Mg/MgO thin film observed along [100] zone axis, layered structure of the compound is clearly observed by *Z*-contrast as bright zig-zag spots (La) and arrays of dumbbells (Cu-Se) in between. At the film-substrate interface, we found that a peculiar atomic structure that has a different layer stacking from the bulk LaCuOSe is formed. From first principles calculations of interfacial adhesive energies, it was found that the different La layers at the interface plays a key role in stabilizing the interface [4]. Similar interfacial structure was observed in LaFeAsO/MgO thin films as well. Another interesting microscopic feature which may be responsible for the transport properties of the LaCuOSe thin film was found by high resolution TEM and STEM observations (FIG. 1). We observed linear contrasts along the parallel direction of the layer stacking. HAADF-STEM observation revealed that those are attributed to planer defects composed of Cu and Se deficiencies (FIG. 1. (b), (c)). These observations are supported by the results of first principles calculations that suggest the production of Cu and Se defects. These defected structures are considered to be possible cause of the hole doping in the present system [5] [6].

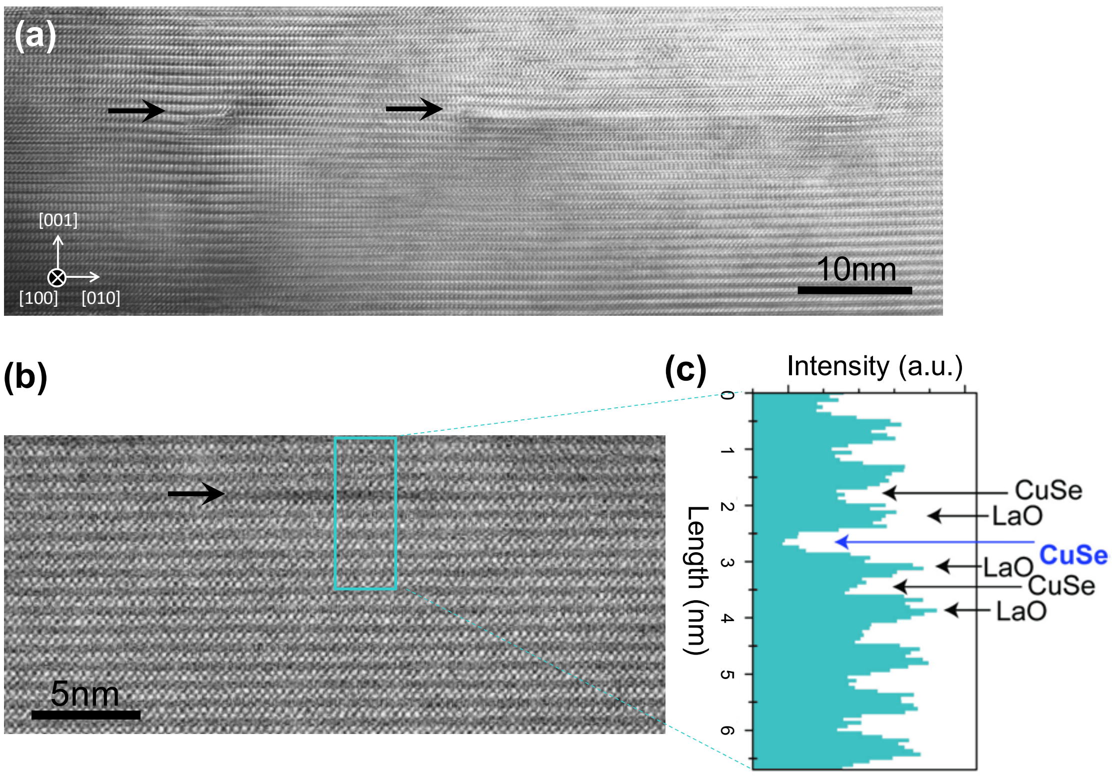

FIG. 1. (a) HRTEM image of LaCuOSe:Mg thin film observed along [100] zone axis. (b) Magnified HAADF-STEM image around a planar defect. Horizontal black arrows in the images indicate planar defects. (c) Intensity profile taken from the square region in the STEM image.

References

[1] H. Hiramatsu *et al.*, Appl. Phys. Lett. **91** (2007) 012104

[2] Y. Kamihara *et al.*, J. Am. Chem. Soc. **130** (2008) 3296

[3] H. Hiramatsu *et al.*, Appl. Phys. Lett. **93** (2008) 162504

[4] T. Tohei *et al.*, Mater. Sci. Eng. B **173** (2010) 229

[5] H. Hiramatsu *et al.*, J. Am. Chem. Soc. **91** (2010) 012104

[6] This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "Nano Materials Science for Atomic Scale Modification 474" from the MEXT, Japan and conducted in the Center for Nano Lithography and Analysis, University of Tokyo.