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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　博士（工学）　氏名　陳　斌杰

学 位 論 文 題 名

Study on the Epitaxial Strain Effects on Optoelectronic Properties of Functional Oxides with Rutile Structure

（ルチル構造を有する機能性酸化物の光電子特性に及ぼすエピタキシャル歪の効果に関する研究）

Rutile-structured oxides (MO_2, space group: $P4_2/mnm$) are known that exhibit diverse optoelectronic properties such as photocatalytic activity, gas sensing properties, transparent conductivity, etc [1-6]. For example, TiO_2 is a well-known photoelectrode material for water splitting. The energy level of the conduction band minimum and the valence band maximum is appropriate for water splitting through photo-excitation-induced band-to-band transition [4]. Electron-doped SnO_2 is a well-known transparent conducting oxide owing to its large optical bandgap and the small carrier effective mass [5]. VO_2 exhibits monoclinic-to-rutile phase transition at T_c ~68 °C. The monoclinic phase is IR transparent insulator and the rutile phase is IR opaque metal. Therefore, VO_2 is a promising candidate for thermochromic materials [6]. The potential applications of these rutile-structured oxides are highly dependent on their optoelectronic properties.

Generally, there are various ways to modulate the optoelectronic properties of a material, each with its own suitability and advantages. In the case of VO_2, reducing the T_c to around room temperature is crucial. Chemical doping of higher valance cations than V^{4+} (e.g. Nb^{5+}, W^{6+}, etc.) [7], field effect regulation [8], and introducing lattice strain [9] have been proposed. In 2002, Muraoka and Hiroi reported that the epitaxial VO_2 film grown on (001) TiO_2 substrates shows an abrupt IMT with reduced T_c around room temperature (25 °C). Therefore, the strain effect from (001) TiO_2 substrates was considered the most effective way to reduce T_c of VO_2 film. Still, there are two limitations for use of TiO_2 substrate: On the one hand, the use of TiO_2 substrate is not realistic in large-scale applications like the smart window because of the size limitation of Verneuil-grown TiO_2 crystal. On the other hand, the film thickness is limited due to strain relaxation through crack formation [10].

To address the difficulties in the practical application of VO_2, and further investigate the strain effects on the optoelectronic properties of VO_2 as well as other rutile-type oxides, in this thesis, I selected M-plane α-Al_2O_3 (M-sapphire) substrate for the epitaxial growth of VO_2, TiO_2, and SnO_2 films. There are several reasons: First, large-scale α-Al_2O_3 substrate has been already industrialized. Second, the M-sapphire was verified to allow the growth of *c*-axis-oriented rutile-structured films. By fabricating VO_2/TiO_2 bilayer on M-sapphire substrate, the effectiveness of M-sapphire substrate to reduce the T_c of VO_2 was verified. Then, I additionally investigated the methods to suppress strain relaxation and crack formation of VO_2 film grown on TiO_2 substrate. Furthermore, noting that M-sapphire shows anisotropic in-plane lattice parameters, which provide a possibility to introduce strain-induced orthorhombic distortion. Based on this, I systematically studied the effects of such distortion on the optoelectronic properties of VO_2, TiO_2, and SnO_2 films. This thesis is composed of the following chapters:

In chapter 1, the background and purposes of related studies are introduced.

In chapter 2, I report the strain effects on the IMT behaviors of VO_2/TiO_2 epitaxial bilayer films grown on M-sapphire substrate [11]. A systematic study with varied thicknesses of TiO_2 and VO_2 layer is conducted. By changing the VO_2 thickness from 40 to 5.5 nm while fixing the TiO_2 thickness to 200 nm, the T_c gradually decreased from 320 K to 305 K, which is highly reduced compared to that of bulk VO_2, suggesting that TiO_2-buffered M-sapphire substrate plays a similar effect to the TiO_2 substrate. Note that orthorhombic distortion is introduced to the film due to the anisotropic lattice parameter of M-sapphire substrate in the in-plane directions. Such distortion is enlarged when reducing TiO_2 thickness, resulting in the suppression of IMT behavior.

In chapter 3, I propose a solution for the strain relaxation and crack formation of VO_2 film grown on TiO_2 substrate. A TiO_2 strain compensation layer (SCL) was inserted between two VO_2 layers to maintain the strain condition of VO_2. The recovery of abrupt IMT behavior and absence of cracks suggest that high strain condition of VO_2 is maintained when TiO_2 thickness exceeds 9 nm. By further alternately stacking VO_2 and TiO_2 layers, I demonstrate that the use of TiO_2 SCL is useful to maintain clear clockwise IMT behavior even when the overall VO_2 thickness is ~50 nm, far thicker than the theoretical thickness (T_c ~15 nm) of VO_2 relaxation.

In chapter 4, I report the effects of orthorhombic distortion on the properties of rutile TiO_2 films. I fabricated 0.5% Nb:TiO_2 films on M-sapphire substrate [12]. By varying the thickness ranging from 300 to 10 nm, the degree of orthorhombic distortion (lattice parameter, b/a) was regulated from ~1.01 to ~1.035. Correspondingly, the carrier effective mass (m^*) decreases from 35 m_0 to 3 m_0 (m_0: electron mass) but the optical bandgap increases, suggesting the optoelectronic properties of rutile TiO_2 is modulated by introducing the lattice distortion.

In chapter 5, I report a comparison study between TiO_2 film and SnO_2 film grown on M-sapphire substrates. Nb:TiO_2 film is distorted as shown in chapter 4, indicating the strained condition, whereas the lattice parameters of SnO_2 films are consistent with the bulk value, suggesting complete strain relaxation. STEM observation revealed that the complete strain release of SnO_2 is due to the combination of large mismatch-induced high strain relaxation and the negligible mismatch-induced strain absence. By contrast, the moderate mismatch between TiO_2/VO_2 and substrate results in the strained condition. Correspondingly, their properties are significantly regulated.

In chapter 6, the above studies are summarized.

In short, I systematically studied the epitaxial strain effects on optoelectronic properties of rutile-structured VO_2, TiO_2, and SnO_2 epitaxial films. The related results would provide useful guidance for the property design of rutile-type oxides and the development of related devices.

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