

STUDY ON THE MOLECULAR BEAM EPITAXIAL GROWTH OF SnO₂ ON Si (001) SUBSTRATE

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Abstract

This work reports the growth of tin dioxide (SnO₂) on Si (001) substrate by molecular beam epitaxy (MBE) technique. The growth mechanism was investigated in-situ by low energy electron microscopy (LEEM). The chemical states and composition of the grown layers were confirmed by X-ray photoelectron spectroscopy (XPS). The morphology was also studied by atomic force microscopy (AFM). The result shows the morphology of grown layers as a particle of about 80 nm in diameter distributed on the substrate like the Volmer-Werber island growth mode. The result shows the possibility to create the island of tin oxide structures on the surface.

Keywords: Tin dioxide, growth mechanism, LEEM, MBE, AFM

Introduction

Tin dioxide is a wide bandgap semiconductor material which has many interesting properties such as high conductivity, high performance for optical transmittance in visible light and near ultraviolet range (Bendjedidi *et al.*, 2015; Jain *et al.*, 2017). In addition, tin dioxide is less toxic, more stable and low cost. Thin films of tin dioxides are therefore attractive in various applications such as gas sensor (Das and Jayaraman, 2014), solar cell (Yang *et al.*, 2018), transparent conducting electrodes (Yu *et al.*, 2014; Fauzia *et al.*, 2017).

Various techniques have been employed for the growth of SnO₂ thin film, for example, spin

coating (Bahade *et al.*, 2017), sputtering (Bai *et al.*, 2019) sol-gel (Javed *et al.*, 2019), chemical vapor deposition (Yu *et al.*, 2019), thermal oxidation (Kwoka *et al.*, 2017) and molecular beam epitaxy (MBE) (Chakraborty and Menon, 2019). Molecular beam epitaxy (MBE) is a technique which can grow high quality thin film with precise control of compositional profiles over the growth process (Franchi, 2013; Morresi, 2013). Despite its potential on the growth of metal oxide thin films, only few studies have been reported on the growth of SnO₂ by MBE (Han *et al.*, 2019; Nikiforov *et al.*, 2020).

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In this work, we report the growth of tin dioxide film on Si (001) wafer substrate by MBE, which can be performed by deposition of Sn and subsequent oxidation in air. The growth mechanism was studied in-situ by low energy electron microscopy (LEEM) and low energy electron diffraction (LEED). The grown tin dioxide film was characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), and X-ray Photoelectron spectroscopy (XPS).

Experiment

Tin dioxide film was grown on Si (001) substrate by MBE at the end station of BL3.2b: Photoelectron Emission Microscopy (PEEM), Synchrotron Light Research Institute (SLRI), Thailand. Tin powder (99.99%, sigma aldrich) was used as source material. Prior to the growth, the Si (001) substrate with the size of approximately 1×1 cm² was cleaned by flashed annealing at 1,050°C. No chemical treatment was performed. The cleanliness and quality of the substrate was checked by LEED. Sn was firstly deposited by heating the source material in a tungsten crucible to approximately 1,000°C. This was done by the electron beam evaporator. The parameters for the evaporator are as follows, high voltage of 1kV, emission current of 12 mA, filament current of 6.5A, and flux current of 50 nA. During the deposition, the substrate was heated and maintained at the temperature of 225°C. The growth was real-time monitored in-situ by LEEM and LEED with bias voltage -20 kV. The deposition was carried out for 3 h under the pressure of less than 5×10⁻⁹ mbar. After the deposition, the obtained sample was exposed to air for 15 min for dry oxidation under the atmosphere.

The surface morphology of the grown sample was studied ex-situ by AFM (Park Systems AFM XE-120) in non-contact atomic force microscope mode and SEM (FEI-quanta 450). The phase analysis and crystalline structure were confirmed by X-ray Diffraction (XRD), Rigaku (Smart Lab), CuK α Radiation ($\lambda = 1.54059\text{\AA}$), in the 2θ range from 10° to 65°. The chemical composition was investigated by XPS (PHI5000 Versa ProbeII) at the SUT-NANOTEC-SLRI joint research facility, SLRI, Thailand. The AlK α (1,486.6 eV) radiation was used as excitation source.

Results and Discussion

The LEED pattern and LEEM images during the growth are shown in Figure 1. Prior to the growth the clear (2×1) (1×2) LEED pattern. was observed within start voltage 30 V. The LEEM image showed the clean and smooth surface of Si (001). After the growth of 1 h, the intensity of the LEED pattern decreased, and the LEED pattern started changing. The LEEM images also showed the rough surface. There was the formation of particles distributed over the surface.

The density of particles increased with the growth time. After the growth for 3 h, the (2×1) and (1×2) diffraction patterns were faded, while the (1×1) diffraction pattern was still clearly observed. This result suggests that the Sn layers were deposited but did not completely cover the substrate surface. The formation of cluster or island of particles was also observed in the LEEM image as shown in Figure 1(h). The size of the island was approximately 100 nm.

After the growth process, the surface morphology of the grown sample was studied by ex-situ SEM and AFM. The SEM image (top view

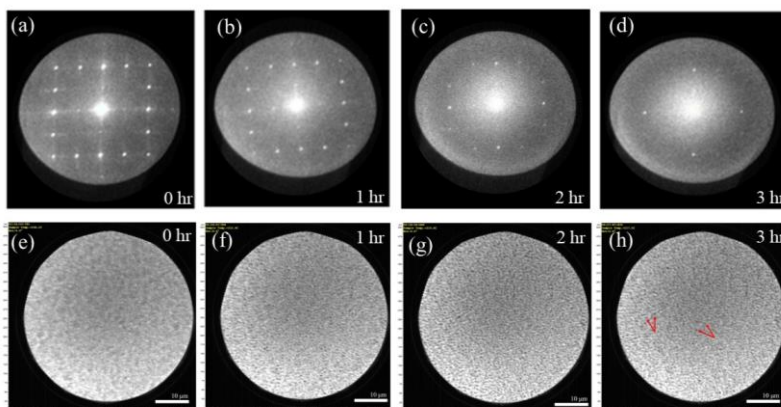


Figure 1. LEED patterns (a-d) and LEEM images (Field of view = 50 μm) (e-f) during the growth process

image) of the grown sample as shown in Figure 2. The SnO_2 island can be seen as bright disks. The top view and 3-dimensional AFM images of the grown samples are shown in Figure 3. The top view image shows the formation of three-dimensional clusters or island of grown layer on the surface. The surface coverage is approximately 20% of the surface the observed clusters have the average size and height of approximately 80 ± 10 nm and 6 ± 2 nm, respectively. This result suggests that the growth follows the Volmer-Werber island or Stranki-Krastanov growth mode (Venables, 2000). This is because the Sn atoms strongly bond with themselves rather than with Si (001) substrate and there is a large compressive strain due to highly mismatched between grown layer and substrate (lattice mismatch of 9%).

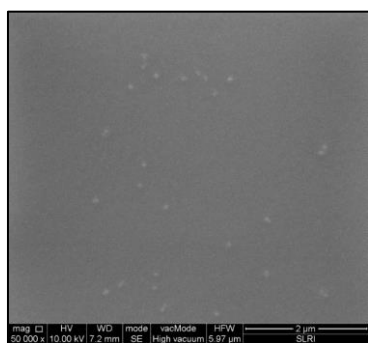


Figure 2. SEM image of the grown SnO_2 on Si (001) substrate film

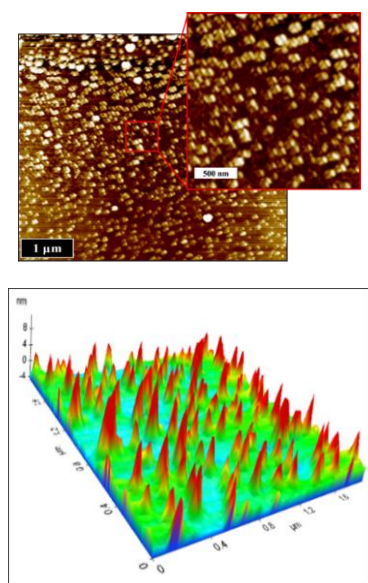


Figure 3. Top view and 3-dimensional AFM images of the grown SnO_2 on Si (001) substrate film

The crystal structure of the grown sample was determined by XRD as shown in Figure 4. The XRD pattern showed only the strong diffraction peaks at $2\theta = 33.0^\circ, 37.0^\circ$ and 61.7° correspond to the (111), (200), and (400) planes of Si, respectively (Neaosuphap *et al.*, 2020). Non crystalline phase of SnO_2 was observed suggesting that the grown sample was formed in amorphous phase.

The chemical composition of the grown sample was investigated ex-situ by XPS. The XPS spectra of the grown sample after exposure to air are shown in Figure 5. The survey spectrum reveals the presence of Sn, O, Si, C on the surface. The presence of C on the surface is due to the surface contamination. The high-resolution spectrum of Sn 3d 5/3 peaks can be deconvoluted into two components at the binding energies of 485.3 eV and 486.9 eV which are attributed to Sn metal (Sn-Sn) and Sn oxide (SnO_2), respectively (Kim *et al.*, 2019). The high-resolution spectrum of O1s peak can be fitted into two peaks at the binding energies of 531.69 eV and 532.93 eV which are assigned to Sn-O and Si-O, (Kwoka *et al.*, 2005), respectively. This result suggests that the grown layer is oxidized after exposure to air and the SnO_2 layer is formed on the surface. The calculated relative atomic concentration of the elements is presented in Table 1. The atomic content between Sn metal and Sn oxide is 90%:10% suggesting that the grown layer is still not completely oxidized to SnO_2 after exposure to air as shown in Figure 6.

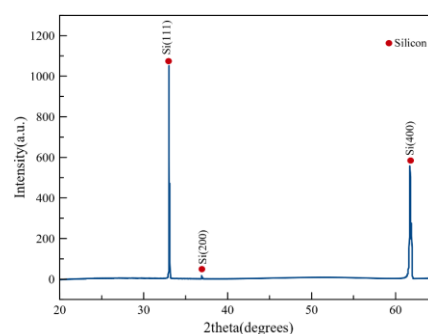


Figure 4. XRD patterns of the grown SnO_2 on Si (001) substrate film

Table 1. Relative atomic concentration of distribution function groups calculated from XPS peak

sample	Relative atomic concentration (%)			
	Sn		O	Si
	5.92		33.12	60.96
	Sn metal	SnO ₂	SnO ₂	SiO ₂
	0.59	5.33	11.64	21.48

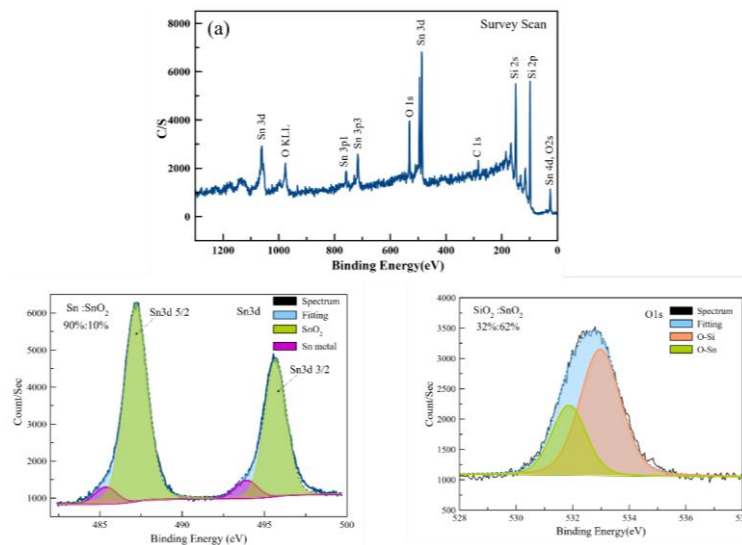


Figure 5. Survey XPS spectrum (a) and high resolution XPS spectra in the Sn3d (b) and O1s (c) regions of the grown SnO₂ on Si (001) substrate film

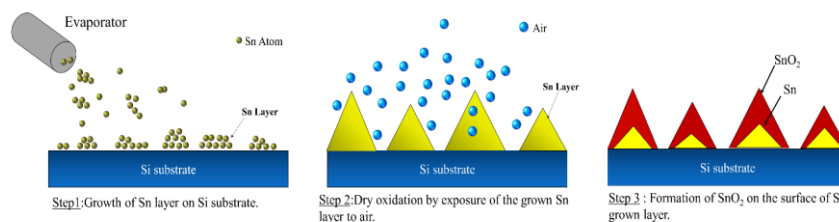


Figure 6. Schematic diagram of the growth process

Conclusions

In summary, the SnO₂ film was grown on Si (001) substrate by MBE technique. The experiment was carried out by deposition of Sn layers and subsequent oxidation in air. The growth mechanism was monitored in-situ by LEEM. The surface morphology of the grown film was studied ex-situ by AFM. It was observed that the growth follows the Volmer-Werber island or Stranki-Krastanov island growth mode. The formation of three-dimensional of the grown layer with the size of approximately 80 nm was observed. The chemical composition of the grown SnO₂ film was confirmed by XPS.

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