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Full Length Article

Ellipsometric study on temperature dependent optical properties of topological bismuth film

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ABSTRACT

Optical properties of bismuth (Bi) film in function of temperature have been investigated by spectroscopic ellipsometry (SE). The solid-liquid phase transition point of Bi thin film is found to be ~262 °C, lower than that of bulk Bi (271.3 °C). The interband transitions of solid Bi occur at 1.82, 3.02 and 4.00 eV, respectively, obtained from imaginary part of dielectric functions and absorption coefficient, which are also consistent with the fitting ellipsometric parameters of the oscillator center energies. A conspicuous difference of optical properties is revealed between solid and liquid Bi, whose characters are semimetal-like and metal-like, respectively. The free electron density of liquid Bi is 10^4 times higher than that of solid Bi. The optical properties of liquid Bi film are mainly influenced by free electrons instead of bound ones. However, with the temperature rising, the increase of both direct and indirect band gaps accords with the characteristics of semiconductor, which can be ascribed to the topological properties of Bi film. This work shows the unique advantage of SE on characterizing the optical properties of topological insulators.

1. Introduction

Bulk bismuth (Bi) is a kind of semimetals, melts at 271.3 °C and boils at 1560 °C. The large temperature range between low melting point and high boiling point makes Bi an excellent candidate for the investigation of liquid metals. Solid-liquid phase transition of Bi transforms the crystal structure from the rhombohedral class of the hexagonal system to some class of the cubic system [1,2]. When reaching melting point, liquid Bi is capped by a single atomic layer denser than bulk Bi [3] and more compact than solid Bi [4], leading to variations in capacity [5], resistance [6], etc. As temperature continues rising, liquid–liquid phase transition takes place at 740 °C [7,8]. New instruments of femtosecond X-ray diffraction [9] and ultrafast ellipsometric pump-probe [10] are employed to observe the phase transition process and liquid metal surface directly. The solid-liquid phase transition of Bi nanoparticles contributes to fabricating the wavelength-selective thermo-optical modulators [11–13]. Moreover, the tunable plasmonic properties of nanostructural Bi achieved through interband transitions have enormous potential applications in metamaterials [14,15]. Optical detection of intrinsic properties is carried out by light-matter interaction, and needs no special treatment on samples with the characteristics of non-contact, non-destructive, etc., when compared with other measurements. Spectroscopic ellipsometry (SE) provides a useful route for the characterization of topological insulators. Electrical and thermal properties of Bi have been widely studied [16–19]. Optical properties of Bi film in liquid and solid phase have also been obtained separately, metal-like liquid Bi typically described with the Drude model [20,21], which has an unambiguous difference with solid Bi [22]. However, to our knowledge, the study of temperature-dependent optical properties for Bi film is rather limited.

This work intends to study the optical property changes in solid-liquid phase transition of Bi film. SE is employed to characterize the optical properties of Bi film at different temperatures from solid phase to liquid phase. The structural and compositional analyses are carried out by X-ray diffraction (XRD). Surface morphology and thickness of Bi film are inspected by atomic force microscopy (AFM) and field emission scanning electron microscopy (FE-SEM).

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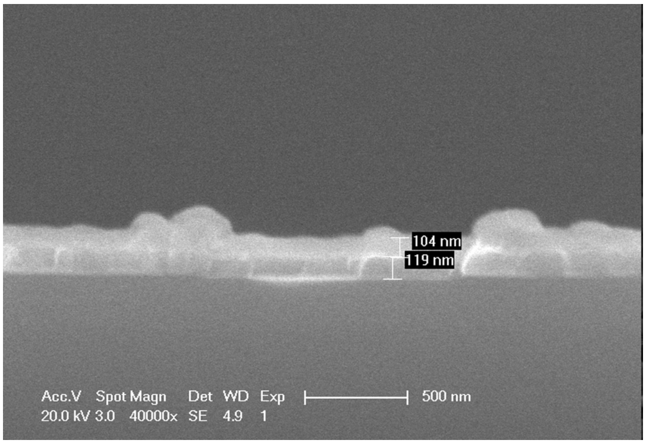

Fig. 1. FE-SEM image of Bi-SiO$_2$ bilayer film.

2. Experiment

The Bi films were deposited onto n-type (100) silicon substrates (99.99% in purity) by electron beam evaporation (EBE) method [23,24]. Before deposition, the substrates have been cleaned with three different solutions, alcohol, acetone and de-ionized water successively for 15 min in ultrasound atmosphere, and then washed with HF solution for 30 s to remove any native oxide material. Because pure Bi can be oxidized during continuous heating in air, SiO$_2$ film was capped on top of pure Bi film as the anti-oxidation layer due to its negligible absorption character in visible range. Two types of samples were prepared, one for pure Bi film, and the other coated with a compact SiO$_2$ layer on it. Thickness of the Bi-SiO$_2$ bilayer film was measured by FE-SEM (HITACHI, FE-SEM-4800-1). A self-established rotating-polarizer-analyzer ellipsometer (RPAE) [25,26], was used to obtain the ellipsometric parameters Ψ and Δ with a precision of 0.005° and 0.01°, with a wavelength range of 300–800 nm (10 nm interval) at 65°, 70° and 75°, respectively. A temperature control system (SKG, AT-908/908P) was employed to measure temperature-dependent ellipsometric parameters, from room temperature (RT) to 270 °C with 0.1 °C measurement precision. The structure and crystalline properties were revealed by XRD (D8 advance, Bruker) using copper Kα_1 as the incident radiation. Surface topography was viewed by AFM (Veeco, VT1000) in non-contact mode with scan range of 2 μm × 2 μm. FE-SEM image and optical properties of Bi at different temperature and energy were acquired from Bi-SiO$_2$ bilayer film. The XRD pattern of pure Bi film at RT was used to contrast that of Bi-SiO$_2$ bilayer film after high temperature measurement. Furthermore, the single wavelength SE measurement of pure Bi film at variable temperature was taken to characterize the phase transition of Bi.

3. Results and discussion

Fig. 1 shows the picture obtained from FE-SEM. The estimated thickness of Bi layer and that of SiO$_2$ layer are 119 nm and 104 nm, respectively. The black line in Fig. 2 shows the XRD pattern of pure Bi film at RT, indicating that Bi is polycrystalline in nature and well-crystallized. Three strong diffraction peaks of textured Bi (003), (006) and (009) reflect that these grain particles preferentially grow parallel to the trigonal axis [001], perpendicular to the film surface [27–29]. The red line in Fig. 2 shows the XRD pattern of Bi-SiO$_2$ bilayer film after high temperature measurement. Obviously, SiO$_2$ layer does have an effect on preventing pure Bi from high temperature oxidation. After high temperature measurement, when compared with XRD pattern of pure Bi film, no BiO$_x$ is observed.

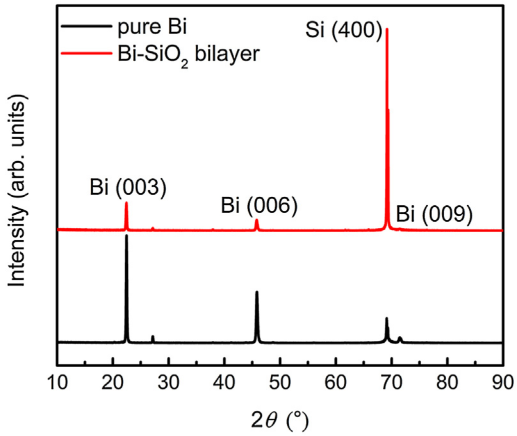

Fig. 2. XRD patterns of pure Bi film at RT and Bi-SiO$_2$ bilayer film after high temperature measurement.

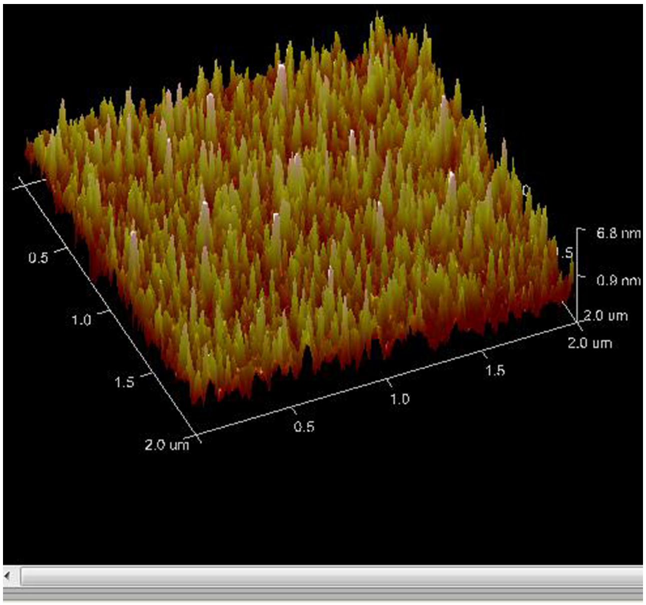

Fig. 3. AFM image of pure Bi film.

The surface topography of pure Bi film viewed by AFM is shown in Fig. 3. In the measured area the root mean square (RMS) 0.79 nm, meaning a smooth and uniform film surface [30,31], makes it appropriate to be characterized by SE [32].

Ellipsometric parameters Ψ and Δ represent amplitude ratio and phase difference of complex reflection coefficients corresponding to the s- and p- polarized light from the film surface, respectively. In order to obtain the optical constants, a four-layer model (air/SiO$_2$/Bi/Si substrate) is employed to fit the ellipsometric parameters. Appropriate optical dispersion models are chosen for all layers. The free electron density of semimetal Bi is 10^5 times lower than those of typical metals. Therefore, a Drude-Lorentz model is employed for Bi layer measured below 250 °C, and it gives [33]

$$\varepsilon = \varepsilon_\infty \left[1 + \sum_j \frac{A_j^2}{(E_{\text{center}})_j^2 - E^2 + iE\nu_j} - \frac{\omega_p^2}{E(E + i\nu_p)} \right] \qquad (1)$$

Drude-Lorentz model is a combination of Lorentz model and Drude model. Lorentz model describes the interaction between light field and bound electrons. ε_∞ shows the high-frequency

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