MBE-grown Bi$_2$Te$_3$ thin films as an efficient hydrogen evolution electrocatalyst

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Abstract

The development of efficient and non-noble metal electrocatalysts with excellent durability for the hydrogen evolution reaction (HER) has attracted increasing attention over recent years. But due to the sluggish water dissociation kinetics as well as the poor long-term stability of most of the existing catalysts, so far it is still a big challenge to achieve efficient low-cost electrocatalysts. It is well-known that surface states are extremely important in catalytic chemical process. Recently, the exotic and robust metallic surface states of topological insulators (TIs) show promising properties as a platform for novel surface chemistry and catalysis. However, research aiming to use TIs as functional electrocatalysts for HER in water splitting applications is still an unprecedented field. In this work, we fabricated Bi$_2$Te$_3$ thin films on ZnSe/GaAs (111)B substrates by the molecular beam epitaxy technique. We demonstrate their high performance as a catalyst in HER by characterizing their onset overpotential, Tafel slope and charge-transfer resistance. The 48 nm Bi$_2$Te$_3$ thin film exhibits an overpotential of 24.9 mV at 10 mA cm$^{-2}$, Tafel slope of 46.69 mV/dec and charge-transfer resistance of 7.7 Ω cm$^2$ with good long-term stability, showing a high potential in electrocatalytic applications. Theoretical studies on their underlying mechanism on their superior performance are underway.

Introduction

The lack of a cost-effective replacement for Pt has plagued the scale of hydrogen electrochemical production (2H$^+$+2e$^-$→H$_2$) for decades; the alternative catalytic materials are fundamentally limited by either a low catalytic efficiency or a short lifetime [1, 2].

Topological insulators (TIs) have been regarded highly promising for various applications because of their fascinating band structure [3, 4], which include an insulator along the c-axis in the bulk state but with the metallic phase along the layer surface [5-7]. The strong spin-orbit coupling in TIs reduces the probability of the electrons in the topologically protected surface states being backscattered by surface defects. As the contamination of the surface of a catalyst is one of the problems in rendering it inactive, topological materials can help overcome this problem because of their protected robust surface states [8, 9]. Theoretical and experimental studies have indicated that materials with their topological surface
state (TSSs) are promising catalysts for chemical processes [10-14]. For example, Xiao et al. studied the effects of TSSs on the activity of transition metal clusters fabricated on a Bi$_2$Se$_3$ substrate using the framework of density functional theory (DFT), and confirmed the HER reactivity of these clusters can gain a positive effect from the TSSs of Bi$_2$Se$_3$ [10]. Yan et al. revisits the surface states on the surface of Au (111) by ab initio band structure calculations and found that they are topologically derived surface states, which are robust against scattering and defects.[11]. Experimentally, He et al. reported that the topological surface states from Bi$_2$Te$_3$, being delocalized and robust owing to their topological natures, can act as an effective electron bath that significantly enhances the surface reactivity of Pd [12]. Rajamathi et al demonstrated the combination of robust topological surface states and large room temperature carrier mobility of Weyl semimetals is a recipe for high activity of HER catalysts [13]. This research group recently reported the photochemical H$_2$ evolution activity with bismuth chalcogenides based TIs in bulk and nanosheet form can promote the hydrogen evolution in photochemical reaction [14]. However, to the best of our knowledge, the research on TI materials directly being used as electrocatalysts in HER with high performance has not been reported so far.

In this work, Bi$_2$Te$_3$ thin films were grown on ZnSe/GaAs(111)B substrate by molecular beam epitaxy (MBE) technique. Their structural characterizations were performed using HRXRD, TEM and AFM. These thin films exhibit low onset overpotential, low Tafel slope, low charge-transfer resistance and high long-term stability in HER.

**Results**
Figure 1 displays the HRXRD spectrum of a typical Bi$_2$Te$_3$ sample. As can be seen, all the Bi$_2$Te$_3$ layer peaks can be indexed as (00l) direction and their measured 2θ values give a c-lattice parameter of ~30.42 Å, which closely matches the standard value of Bi$_2$Te$_3$ (c=30.483 Å). While for the two ZnSe buffer peaks, their measured 2θ values deduces a lattice constant of ~5.658 Å, which agrees well with the known lattice constant of ZnSe (a=5.669 Å).
Figure 2 Cross-sectional TEM images of Bi$_2$Te$_3$ thin films with thicknesses of a 6 nm, b 34 nm, c 48 nm and d 61 nm. The insets of Figure 2a-d are Fast Fourier transform (FFT) patterns of Bi$_2$Te$_3$.

The cross-sectional TEM images of the Bi$_2$Te$_3$ samples studied in this work are shown in Figure 2. It can be seen that each of the four samples consists of a 7 nm ZnSe buffer layer, and the thicknesses of Bi$_2$Te$_3$ thin films are determined to be 6 nm, 34 nm, 48 nm and 61 nm. The FFT patterns shown in the insets of Figure 2 reveal that two sets of hexagonal lattice appear in these thin films, indicating the existence of twin crystals [15], attributed to the fact that (00l)-oriented Bi$_2$Te$_3$ has a 3-fold symmetry, while the GaAs (111) substrate has a 6-fold symmetry.
AFM images of the surfaces of the four Bi$_2$Te$_3$ samples with different magnification are shown in Figure 3. Figure 3a-c are the AFM images of the 6 nm Bi$_2$Te$_3$ thin film, in which the rough surface contains no observable domains, perhaps it is because the film is too thin. Figure 3d-f are the AFM images of the 34 nm Bi$_2$Te$_3$ thin film, in which triangular domains can be seen. In Figure 3f, one can see that smaller triangular domains are being developed on top of the larger domains through the spiral growth mode. Figure 3g-i are the AFM images of the 48 nm Bi$_2$Te$_3$ thin film, which show that all the smaller triangular domains have been developed fully so that this sample has the highest density of the domain structure. Figure 3j-l are the AFM images of 61 nm Bi$_2$Te$_3$ thin film, in which the triangular domains seem to getting merged with each other, as an evidence that the growth of Bi$_2$Te$_3$ at the places between the domains have already been initiated after the growth of the smallest triangular domains was completed. As shown in the profile analysis of Figure 3f and 3i for the layers across a spiral growth path, each layer has a height approximately equal to 1 nm, in good agreement with the thickness of a single QL Bi$_2$Te$_3$. 

**Figure 3.** AFM images of Bi$_2$Te$_3$ films with thickness a-c 6 nm, d-f 34 nm, g-i 48 nm and j-l 61 nm.
Figure 4. HER Electrochemical performances of MBE-grown Bi$_2$Te$_3$ thin films. a) LSV polarization curves (iR-corrected) of as-grown Bi$_2$Te$_3$ with different thicknesses, ZnSe buffer, n+GaAs substrate and commercial Pt. b) Corresponding Tafel plots of the active materials in a. c) LSV Polarization curves (iR-corrected) of 48 nm Bi$_2$Te$_3$ film recorded before and after 5000 cyclic voltammetry. d) Chronoamperometry (CP) test results of the 48 nm Bi$_2$Te$_3$ thin film and commercial Pt. e,f) Electrochemical impedance spectra of the active materials in a.

Table 1. Comparision of the HER performances of Bi$_2$Te$_3$ films, reported exfoliated Bi$_2$Te$_3$ and MX$_2$-based catalysts. The electrolytes are all 0.5M H$_2$SO$_4$.

| Catalyst                        | $\eta$ (mV vs. RHE) for $j=-10$mA cm$^{-2}$ | Tafel slope (mV/dec) | References |
|---------------------------------|--------------------------------------------|----------------------|------------|
| Bi$_2$Te$_3$ film (48 nm)       | 249                                       | 46.69                | This work  |
| Exfoliated Bi$_2$Te$_3$         | 680                                       | N/A                  | [16]       |
| 2H-MoS$_2$/Au (111)             | 250                                       | 55-60                | [17]       |
| 2H-MoS$_2$ bicontinuous network | 285                                       | 50                   | [18]       |
| MoS$_2$ flakes                  | 250                                       | 70                   | [19]       |
| 2H-MoS$_2$                     | 343                                       | 82                   | [20]       |
| P-2H-MoS$_2$+S                 | 257                                       | 62                   | [20]       |
| V-MoS$_2$ (EC)                 | 320                                       | 102                  | [21]       |

We have examined the HER electrochemical catalytic behaviors of the as-grown Bi$_2$Te$_3$ films, as well as the ZnSe buffer and an n+GaAs substrate. Figure 4a displays the LSV (linear sweep voltammogram)
polarization curves of these active materials, as can be seen, the overpotentials ($\eta$) of the Bi$_2$Te$_3$ thin films at a cathodic current density ($j$) of 10 mA/cm$^2$ ranged within 249-380 mV. It is well known that the MX$_2$ (molybdenum dichalcogenide) are among the most promising non-noble metal catalytic materials for HER. For comparison the onset overpotentials of Bi$_2$Te$_3$ films in this work as well as those of exfoliated Bi$_2$Te$_3$, MX$_2$ based catalysts displayed in Table 1 [16-21]. As shown in Table 1, our 48 nm Bi$_2$Te$_3$ thin film is among the active materials with the lowest overpotential and it indeed outperforms the exfoliated Bi$_2$Te$_3$ (680 mV).

The corresponding Tafel plots of the curves shown in Figure 4a are displayed in Figure 4b. The linear portions of these plots are fitted to the Tafel equation ($\eta$=blog+j+a, where $j$ is the current density and $b$ is the Tafel slope), yielding Tafel slopes of 38.89, 46.69~57.88, 327.56 and 347.12 mV/dec for Pt, Bi$_2$Te$_3$ films, ZnSe buffer and n+GaAs(111)B substrate, respectively. It is worth to mention that the Tafel slope (~46.69 mV/dec) of the 48 nm Bi$_2$Te$_3$ films is close to that of Pt (~38.89 mV/dec).

Figure 4c shows the polarization curves of the 48 nm Bi$_2$Te$_3$ thin film recorded before and after 5000 cyclic voltammetry treatments. As can be seen in this figure, there is no obvious potential decay after the cyclic treatments, indicating that HER electrochemical process does not cause substantial changes in the structure and composition of the film.

In addition, the results of chronoamperometry test performed on this film, as shown in Figure 4d, manifest that the 48 nm Bi$_2$Te$_3$ films exhibits an outstanding long-term operational stability, comparable to that of commercial Pt, however, the current density versus time curve of our thin film is more stable without the sharp spikes shown in the corresponding curve of commercial Pt, attributed to the much smaller size of the bubbles generated during the HER process in former case.

Figure 4e and f show the results of electrochemical impedance spectroscopy (EIS) measurement performed on the active materials shown in Figure 4a except Pt. By performing the standard data analysis on the Nyquist plots shown in Figure 4e and f and applying a simplified Randles circuit model as shown in Figure 5, we can derived the electrolyte resistance ($R_s$), constant of double layer capacitance ($C_{dl}$) and charge transfer resistance ($R_{ct}$) of the active materials shown in Figure 4a except Pt. The results are shown in Table 2 in which one can see that the 48nm Bi$_2$Te$_3$ thin film exhibits the lowest $R_{ct}$ among the four Bi$_2$Te$_3$ thin films a, consistent with the observation that its onset overpotential and Tafel slope being the lowest. We believe the superior performance of the 48 nm Bi$_2$Te$_3$ thin film is likely contributed by the fact that it has the largest surface area and active site among the four films (as shown in Figure 3) during the HER process, which leads to a more efficient interaction between the catalytic surfaces and electrolytes.
Figure 5. Simplified Randles circuit. Equivalent circuit models used for fitting the EIS response of HER, where $R_s$ is the electrolyte resistance, $C_{dl}$ represents the constant phase elements, $R_{ct}$ denote the charge-transfer resistance.

| Material                | $R_s$ ($\Omega \text{ cm}^2$) | $C_{dl}$ (mF cm$^{-2}$) | $R_{ct}$ ($\Omega \text{ cm}^2$) |
|-------------------------|-------------------------------|--------------------------|----------------------------------|
| n+GaAs                  | 3.25                          | 289                      | 1469                             |
| ZnSe buffer film        | 3.12                          | 510                      | 1065                             |
| Bi$_2$Te$_3$ (6 nm)     | 4.312                         | 28.13                    | 17.4                             |
| Bi$_2$Te$_3$ (34 nm)    | 3.858                         | 24.81                    | 12.23                            |
| Bi$_2$Te$_3$ (48 nm)    | 4.081                         | 95.2                     | 7.725                            |
| Bi$_2$Te$_3$ (61 nm)    | 4.765                         | 64.98                    | 8.451                            |

Table 2. The EIS fitting results of Bi$_2$Te$_3$ films, ZnSe buffer and n+GaAs substrate.

**Method**

**Materials synthesis.** All the samples studied in this work were fabricated on GaAs (111)B n+ substrates by a VG-V80H MBE system. For each sample, a 7-nm-ZnSe buffer layer was firstly deposited, followed by the growth of a Bi$_2$Te$_3$ layer with a desired thickness. All the growth processes were performed in an ultra-high-vacuum chamber with a basic pressure better than $1.0 \times 10^{-9}$ torr.

**Materials characterization.** The samples were characterized by HRXRD (X’pert Pro Thin Film, using Cu Kα radiation, and the 2θ scan ranged from 10 to 70°), TEM (JEOL JEM-2010F with an acceleration voltage of 200 kV), and AFM (Digital Instrument Nanoscope IIIa).

**Electrochemical measurements.** All the electrochemical measurements were performed in a three-electrode system connected to a CHI 760E electrochemical workstation (CH Instruments), using Bi$_2$Te$_3$/ZnSe/GaAs (111)B as the working electrode, a Pt foil as a counter electrode, a saturated calomel electrode (SCE) served as the reference electrode, and 0.5 M H2SO4 as the electrolyte(sparged with N$_2$, purity ~99.99%). All the potentials were calibrated by a reversible hydrogen electrode (RHE). Linear sweep voltammetry was performed using a scan rate of 5mV s$^{-1}$, from +0.10 to -0.70 V vs RHE. The Nyquist plots were obtained with frequencies ranging from 100 kHz to 0.1Hz at the overpotential of 10mV. The impedance data were fitted to a simplified Randles circuit to extract the series and charge-
transfer resistances. All data presented were $iR$ corrected, where the solution resistances were determined by EIS experiments.

Conclusion
We have successfully synthesized high-quality Bi$_2$Te$_3$ thin films with different thickness on n+GaAs(111) substrates by molecular beam epitaxy. Their structural properties were examined by HRXRD, cross-sectional TEM and AFM, revealing that the 48 nm Bi$_2$Te$_3$ thin film has the densest distribution of triangular domains. The performance of these thin films as an electrocatalyst in HER was characterized by various electrochemical measurements. It was found that they all show high activity in HER, in particular, the 48 nm Bi$_2$Te$_3$ thin film exhibits the lowest onset overpotential, lowest Tafel slope and lowest charge–transfer resistance, which are among the best values achieved by existing candidates of non-noble metal catalysts. The theoretical studies aiming to reveal the underlying mechanism of the superior HER performance of this topological insulator material are underway.

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