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10.48785/100/81

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Van der Waals epitaxy of C_{60} on the topological insulator Bi_2Se_3

C.S.Knox, M.D.Rogers, T.Moorsom

This application note describes the growth of a novel Bi_2Se_3/C_{60} heterostructure in the Royce deposition system at the University of Leeds. We also present structural characterisation and transmission electron microscopy data in order to understand nature of the Bi_2Se_3/C_{60} interface.

1 Introduction

Bismuth selenide (Bi_2Se_3) has attracted much experimental interest as an archetypal 3D topological insulator, where transport is dominated not by the insulating bulk band alignment, but by metallic, spin-polarised surface states [1]. As long as time-inversion symmetry remains unbroken, these surface states are protected against elastic back-scattering, as such an event would require a spin-flip [2]. Bi_2Se_3 grows with a layered crystal structure, where atomic layers in the sequence Se-Bi-Se-Bi-Se (so-called quintuple layers) are separated by a van der Waals (vdW) gap between the selenium atoms [3]. This allows Bi_2Se_3 to be grown on a wide variety of substrates [1, 4, 5], as the growth is initiated by a vdW gap between the substrate and the Bi_2Se_3 , without the need for a strained interfacial layer, in a process known as van der Waals epitaxy [6]. Additionally, as a Bi_2Se_3 quintuple layer is terminated by a passivated selenium layer, a vdW gap can form between the Bi_2Se_3 and a subsequently deposited material [7]. It has recently been noted that buckminsterfullerene (C_{60}) also orders surprisingly well on a Bi_2Se_3 substrate [8].

Previously, it has been noted that the electronic structure of a C_{60} molecular film is highly substrate dependant, due to charge-transfer induced band broadening [9–11]. However, recent observations of bulk-like C_{60} bands on a Bi_2Se_3 substrate seem to indicate that there is very little hybridisation between the Bi_2Se_3 bulk and the C_{60} [8, 12]. As the molecular orbitals within the C_{60} can be tuned by an applied gate bias [13], this presents an interesting opportunity investigate the hybridisation between the topological surface states and the bands of C_{60} [14, 15].

Here we report on the novel growth of a bilayer Bi_2Se_3/C_{60} heterostructure grown in the Royce thin film deposition system at the University of Leeds. The bulk crystal structure of the Bi_2Se_3 and the C_{60} is probed by Raman spectroscopy and X-ray diffraction measurements, which show that both materi-

als within this heterostructure are well ordered in a strain-free, bulk-like manner. We also examine the Bi_2Se_3/C_{60} interface under transmission electron microscopy (TEM) at the LEMAS facility at the University of Leeds, and determine that while the C_{60} is grown by vdW epitaxy on top of completed Bi_2Se_3 quintuple layers, the existence of bismuth dangling bonds at the edge of a Bi_2Se_3 terrace disrupts the vdW epitaxy of the C_{60} , leading to the formation of a disordered region at the interface.

2 Growth

In preparation for the growth procedure, 8×8 mm [0001] oriented Al_2O_3 substrates were cleaned under ultrasonic agitation in acetone and isopropyl alcohol, in order to remove any possible organic contaminants from the dicing process. The sapphire substrate is then air-dried before being immediately loaded into the Royce thin film deposition system. Once loaded, the substrate was transferred to the Royce MBE system, where it was heated to 500 °C (measured by a thermocouple attached to the sample manipulator) in order to outgas the sample holder and remove any remaining contaminants from the substrate.

The Bi_2Se_3 layer was grown by evaporating bismuth and selenium from standard dual-filament Knudsen cells. The Bi:Se flux ratio, measured by an ion-gauge flux monitor, was maintained at 1:15 throughout the growth, in order to obtain stoichiometric Bi_2Se_3 and to minimise the formation of selenium vacancies [5]. In order to improve the quality of the as-grown Bi_2Se_3 , a two-step process was adopted [1], whereby a thin nucleation layer of Bi_2Se_3 was grown at a lower temperature. For this study, an intentionally low temperature of at 130 °C was chosen, in order to study the effects of surface roughness on the ordering of the C_{60} molecular film [5]. After this nucleation layer was grown the rest of the epitaxial Bi_2Se_3 was grown at a temperature of 330 °C.

The Bi_2Se_3 sample was then transferred through

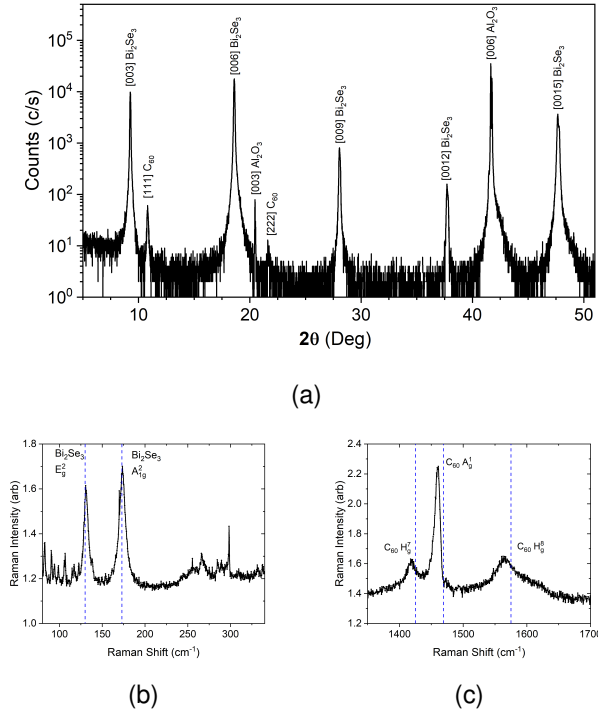


Figure 1: Structural characterisation of the $\text{Bi}_2\text{Se}_3/\text{C}_{60}$ sample. Panel a) depicts the X-ray diffraction spectrum of the $\text{Bi}_2\text{Se}_3/\text{C}_{60}$ sample, where the positions of the known diffraction peaks are labelled with the relevant material and lattice planes. Panels b) and c) show the Raman spectra of the $\text{Bi}_2\text{Se}_3/\text{C}_{60}$ sample, where the blue dashed lines represent the expected positions of the Raman modes. Panel b) shows the low frequency range, dominated by the Bi_2Se_3 modes, as excited by a 633 nm laser. Panel c) shows the high frequency range, dominated by the C_{60} modes, as excited by a 473 nm laser.

the radial transfer chamber under a pressure of $\approx 10^{-11}$ mbar, to the Royce organics chamber. From there, a thick C_{60} layer was grown, over the course of 20 minutes, from a standard Knudsen cell with the Bi_2Se_3 substrate at ambient temperature [16]. This structure was then capped by a 15 nm thick platinum layer, deposited via electron-beam evaporation. The thickness and deposition rate of the platinum film was monitored by a quartz crystal balance.

3 Material Properties

The X-ray diffraction (XRD) spectrum for the $\text{Bi}_2\text{Se}_3/\text{C}_{60}$ heterostructure is shown in Fig. 1a. The sample shows clear Bi_2Se_3 peaks ordered in the [001]

direction, with a c-axis lattice parameter of 2.861 ± 0.007 nm, which is in agreement with the bulk lattice parameter of 2.866 nm [17]. Additionally, we can see that the inter-molecular spacing of the face centred cubic C_{60} lattice is 1.415 ± 0.007 nm, which correlates closely with the lattice spacing for bulk C_{60} , 1.42 nm [18]. This indicates that not only has the Bi_2Se_3 grown epitaxially on top of the Al_2O_3 substrate, but that the C_{60} has grown in a well ordered and relaxed manner on top of the Bi_2Se_3 .

To confirm this observation, the vibrational spectrum of the $\text{Bi}_2\text{Se}_3/\text{C}_{60}$ heterostructure was characterised by Raman spectroscopy. Two spectral ranges were considered, one between 80 and 340 cm^{-1} , which encompasses the principle phonon modes of Bi_2Se_3 (shown in Fig. 1b)[19], and the other between 1200 and 1700 cm^{-1} , detailing the vibrational spectrum of the C_{60} [20] (shown in Fig. 1c). Fig. 1b corroborates the observations from the XRD data, as the sample shows well defined Bi_2Se_3 Raman modes at $131 \pm 1\text{ cm}^{-1}$ and $173 \pm 1\text{ cm}^{-1}$, indicating well relaxed Bi_2Se_3 [19]. The high frequency regime also shows that we have well ordered C_{60} , with C_{60} Raman modes at $1419 \pm 1\text{ cm}^{-1}$, $1460 \pm 1\text{ cm}^{-1}$ and $1566 \pm 1\text{ cm}^{-1}$, which correlate well with the expected positions of the C_{60} H_g^7 , A_g^2 and H_g^8 Raman modes, respectively [21].

In order to discern why the C_{60} would order so well on top of the Bi_2Se_3 film, the $\text{Bi}_2\text{Se}_3/\text{C}_{60}$ interface was examined under transmission electron microscopy (TEM) at the LEMAS facility at the University of Leeds. A scanning electron microscope image of the region examined under TEM is shown in Fig. 2a. The clear, terraced, triangular domains of the underlying Bi_2Se_3 surface are clearly visible through the C_{60} film. We note that, between these triangular domains, there are ≈ 500 nm wide voids in the Bi_2Se_3 film, formed as a result of the excessively low temperature chosen for the nucleation layer of Bi_2Se_3 [5], where the C_{60} has deposited directly on the Al_2O_3 substrate. Examining the entire stack structure under TEM shows that the Bi_2Se_3 is approximately 124 ± 1 nm thick, resulting in an average growth rate of $0.295 \pm 0.003\text{ \AA s}^{-1}$ over the course of the 70 minute deposition procedure. Similarly, the C_{60} is found to be 104 ± 1 nm thick, resulting in an average growth rate of $0.833 \pm 0.008\text{ \AA s}^{-1}$.

When the $\text{Bi}_2\text{Se}_3/\text{C}_{60}$ interface is examined under TEM (as shown in Fig. 2b), we find that not only are the lattice planes of the Bi_2Se_3 and the C_{60} clearly vis-

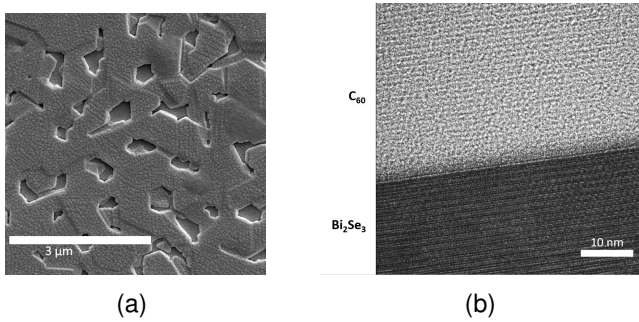


Figure 2: Electron microscopy images of the $\text{Bi}_2\text{Se}_3/\text{C}_{60}$ sample. Panel a) shows a scanning electron microscope image of the sample surface, highlighting the C_{60} grains, as well as the large triangular terraces, characteristic of Bi_2Se_3 growth. Panel b) shows a TEM image of the $\text{Bi}_2\text{Se}_3/\text{C}_{60}$ interface, highlighting the ordered nature of both materials, and the sharp interface between them.

ible, but the $\text{Bi}_2\text{Se}_3/\text{C}_{60}$ interface is sharp, and the C_{60} is well ordered within the first few monolayers, without a strained and disordered interfacial layer. However, if we observe the $\text{Bi}_2\text{Se}_3/\text{C}_{60}$ interface at a terrace edge on top of the triangular Bi_2Se_3 domains, as shown in Fig. 3a, we note that this is no longer the case. In fact, we find that if we take a 2D Fourier transform of the C_{60} where the molecular film is deposited on top of a terrace flat (shown in Fig. 3b), there is a clear 0.79 ± 0.02 nm periodicity, corresponding to the diameter of the C_{60} molecular cage [22]. However, if a similar Fourier transform is attempted at the step-edge of a terrace we find that the clear vertical periodicity is replaced by an amorphous ring with a similar 0.79 ± 0.02 nm periodicity, as shown in Fig. 3c.

The presence of this disordered layer at the $\text{Bi}_2\text{Se}_3/\text{C}_{60}$ interface appears to indicate that some strain is being applied to the C_{60} by the Bi_2Se_3 . This would point to the existence of dangling bonds at the step-edge of the Bi_2Se_3 terrace, which can disrupt vdW epitaxy [4, 23]. At the terrace step-edge there are exposed bismuth atoms, effectively creating a selenium vacancy at the step edge. Previously, it has been noted that selenium vacancies act as n-type donors within Bi_2Se_3 [24, 25]. By freeing additional electrons, these selenium vacancies will result in the formation of dangling bismuth bonds [3]. These dangling bonds are chemically active, and so will bond to the C_{60} molecules, but as the bond angles within the material are limited [6], this will apply strain to the C_{60}

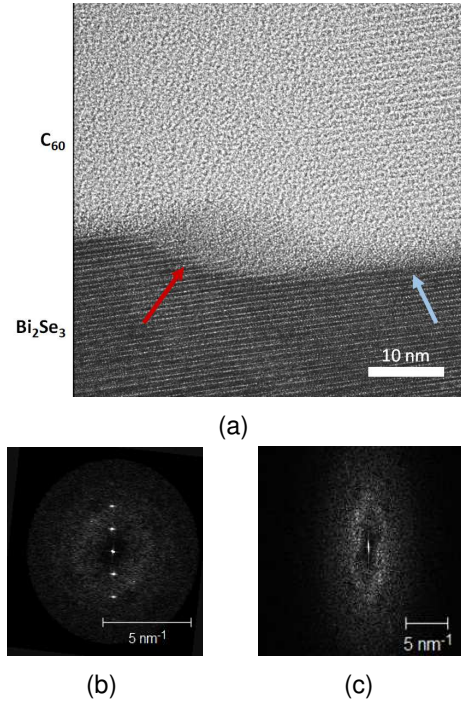


Figure 3: Electron microscopy images of the $\text{Bi}_2\text{Se}_3/\text{C}_{60}$ sample at the terrace edge of a Bi_2Se_3 domain. Panel a) shows a TEM image of the $\text{Bi}_2\text{Se}_3/\text{C}_{60}$ interface around a terrace step. Two regions are highlighted, one where the C_{60} has grown on top of a complete Bi_2Se_3 layer (blue arrow) and another where the C_{60} has grown on top of a terrace step (red arrow). Panels b) and c) show 2D Fourier transforms of the C_{60} within the regions highlighted by the blue and red arrows, respectively.

film resulting in the disordered interface layer seen in Fig. 3a.

We note that our results support those in Refs. [8] and [12]. As C_{60} grows on top of Bi_2Se_3 by vdW epitaxy, only tunnelling events will result in charge transfer between the bulk of the topological insulator and the organic semiconductor [9, 10]. As such, there should be very little hybridisation between the C_{60} bands and the Bi_2Se_3 bulk, as seen for C_{60} in Ref. [8] and Bi_2Se_3 in Ref. [12]. We have also highlighted the need for atomically flat Bi_2Se_3 substrates in potential organic-topological insulator heterostructures, due to the existence of bismuth dangling bonds at the Bi_2Se_3 terrace step-edge.

4 Further Information

The Royce Deposition System is a multichamber, multitechnique thin film deposition tool based at the University of Leeds as part of the Henry Royce Institute. Materials from the Royce Deposition System are available as a facility service and for collaborations.

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