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A modified Wenzel model for water wetting on van der Waals layered materials with topographic surfaces[†]

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A modified Wenzel model is proposed for describing the wetting behavior of van der Waals layered materials with topographic surfaces, based on the measured linear relationship between water wetting and surface roughness for high quality Bi_2Se_3 thin films, synthesized using molecular beam epitaxy (MBE) in the optimized temperature window of 180-200 °C. The water contact angles are found to have apparent dependence on the nanoscale surface morphology, enabling film wettability as a new tool to quickly characterize the quality of atomically thin films. The water contact angle of the ideal Bi_2Se_3 surface is inferred to be ~98.4°, indicating its intrinsic hydrophobic nature; however, the edge of the terrace on its surface is extremely hydrophilic, leading to easy hydrophobic/hydrophilic transitions. The atomistic mechanism is further revealed by first principles calculations. The regulated wettability is of great importance for electronic applications of Bi_2Se_3 and other two-dimensional materials with distinctive electronic structures.

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1. Introduction

Over the past few years, two-dimensional (2D) and van der Waals (vdW) layered materials held by strong intralayer covalent bonds and weak interlayer interaction have been receiving tremendous research interest, due to their exceptional electronic, optical, and magnetic properties.¹ Besides the intensive studies on such properties, the interaction between these materials and their environment, such as the presence of moisture and adsorbates, has also drawn more and more attention, thanks to its critical importance for practical electronic applications.² A ubiquitous adsorbate is water for industrial applications of these materials. It is well known that the intrinsic water wettability on the substrate depends on interfacial interactions dominated by the chemical composition, surface

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topography, and the nature of water-surface bonding.^{3,4} Recently, peculiar wetting behaviors on 2D and vdW layered materials, such as the wetting transparency of graphene sheets,^{5,6} thickness-dependent wettability^{7,8} of transition metal dichalcogenides (TMDs) and wetting formation on hydrophilic/ hydrophobic substrates under ambient conditions in the presence of 2D coating materials^{9,10} have been discovered, implying that specific water-substrate interaction features are relevant to the atomic and electronic structures of layered materials. However, a key challenge for studying wetting on such materials is that a well-defined and completely clean surface is needed. Even the wettability of graphene is largely controversial and is under active debate due to the possible presence of pollutants created during sample transfer and explosion in atmosphere.^{5,11} As a result, despite numerous experiments being reported in the literature, a clear and general physical picture of water wetting on vdW layered materials is still lacking.

On the other hand, due to the layer-by-layer structure, synthesized vdW-layered materials usually adopt topographic surfaces with terrace defects, which play crucial role in device applications. Therefore, it is urgently needed to develop quick and simple methods to characterize the quality of synthesized vdW-layered materials. At present, the most widely employed method is using an index of root-mean-square (RMS) "roughness" characterized by atomic force microscopy (AFM), on the basis of the statistics of height distribution of the triangular terraces, and it is recorded to roughly evaluate the quality of

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[†] Electronic supplementary information (ESI) available: AFM images of SrTiO₃ (111) substrates processed with the same procedures described in the text; the contact angle *versus* RMS roughness; the RMS surface roughness of Bi₂Se₃ films measured from different sized areas; the definition of RMS roughness; and the AFM topography images of Bi₂Se₃ grown at different various substrate temperatures. See DOI: 10.1039/c7nr00521k

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layered materials.¹² There are two main drawbacks of this method. Firstly, the scanning rate of AFM is very slow for a large sample area, which will seriously limit the speed of characterization. Secondly and more importantly, the roughness evaluated by the surface terrace heights is in fact not a good indicator for the description of the quality of layered materials, which will be discussed below. However, if the interaction between water and vdW-layered materials with topographical surfaces is fully understood, it is possible to employ wettability to quickly perform quantitative characterization of the surface morphology for vdW-layered materials.

Motivated by the above facts, we take a Bi_2Se_3 thin film as a particular example to study the general wetting principles for typical vdW-layered materials. Bi_2Se_3 has been widely studied in these years, due to its great potential to be a wide-gap topological insulator (TI).^{13,14} To date, experimentalists have employed synthesis techniques including molecular beam epitaxy (MBE)¹⁵⁻¹⁸ to grow Bi_2Se_3 thin films on various substrates,¹⁷⁻²³ where the growth dynamics of Bi_2Se_3 is found to be extremely sensitive to the temperature, the deposition rate, and the interaction with substrate. In such pioneering work, high density triangular terrace domains are always observed on surfaces,¹⁷⁻²³ indicating that the quality of grown Bi_2Se_3 is difficult to control.

In the present work, we stride to grow high quality Bi₂Se₃ thin films with a series of well-defined surface morphologies by changing the growth conditions using MBE in an ultra-high vacuum, where the pollution affecting wetting can be significantly reduced. Water contact angle (CA) measurements on these clean Bi₂Se₃ surfaces were carried out immediately after removing them from the vacuum chamber. We find that the relationship between triangle-shaped terrace domains and the water contact angles on the Bi₂Se₃ surface obeys a modified Wenzel model, indicating that it is reasonable to employ wettability as a quick and simple characterization for the quality of the synthesized atomically-thin films. The extrapolated CA (~98.4°) shows unexpected high hydrophobicity of the ideal Bi₂Se₃ surface, but the edge of terraces is extremely hydrophilic. Such a huge difference in hydrophobicity between the terraces and stepped edges implies that the hydrophobic/ hydrophilic transition of vdW-layered films can be easily controlled by introducing a small amount of step edges. The present results are important for both fundamental understanding and device applications of vdW-layered materials, since the hydrophobic nature of high quality Bi₂Se₃ thin films enables robust, low-cost, and self-cleaning nanoelectronics and spintronics without sealing. Furthermore, the modified Wenzel model provides a generalized wetting picture for vdW layered materials with terraced topographic surfaces.

2. Methods

2.1 Growth of Bi₂Se₃ thin films

 Bi_2Se_3 thin films were synthesized on $SrTiO_3$ (111) substrates using a home-made MBE system. Similar to that reported by

Zhang *et al.*,²¹ SrTiO₃ (111) substrates were firstly cleaned with ultrasonic agitation subsequently in acetone for 10 minutes, in ethanol for 10 minutes, and in hot deionized water for 40 minutes, respectively. After that, substrates were annealed at 950 °C for 3 hours under a pure oxygen (99.999%) atmosphere, and at the appropriate temperature in the growth chamber before the growth starts. During the growth, high purity Bi (99.97%) and Se (99.999%) were evaporated from Knudsen cells, where the ratio of Bi/Se fluxes was controlled at 1:10 by using a quartz microbalance flux monitor. The typical growth rate of Bi₂Se₃ films was about 0.2 nm per minute in the present experiments.

2.2 Characterization of hydrophobicity

The surface morphologies of Bi_2Se_3 samples were examined by using AFM, where the RMS surface roughness was recorded. Contact angles were measured on a Dataphysics OCA20 contact angle system at room temperature (~293 K). The deionized water droplet size used for measurements was 0.2 µL. To reduce the statistical error, the value of CA was obtained by averaging measurements at three different positions of the same sample.

2.3 First principles calculations

First-principles calculations were performed using the vdW density functional²⁴ in the Vienna *Ab initio* Simulation Package (VASP),^{25,26} combined with projector-augmented wave (PAW) pseudopotentials,^{27,28} as well as the plane-wave basis set with energy cutoff at 400 eV. A 5 × 5 supercell of Bi₂Se₃ thin film with a thickness of two quintet-layers was chosen for calculation of water adsorption on the perfect surface. In the case of water adsorbed on the edged surface, a 4 × 6 supercell was employed, and an edge step was created by cutting the top quintet-layer. Both structures were fully relaxed until the maximum force was less than 0.01 eV Å⁻¹. A vacuum region of \geq 15 Å was applied, and the Brillouin zones were sampled by using 2 × 2 × 1 and 3 × 2 × 1 Monkhorst–Pack *k*-meshes for perfect and stepped Bi₂Se₃ surfaces, respectively.

Results and discussion

3.1 Surface morphology

The quality of substrate plays a key role during the MBE growth of Bi_2Se_3 films. We first carefully checked the configuration of the processed $SrTiO_3$ (111) surface by using AFM. It is found that although the substrate surfaces processed under the same conditions exhibit slightly different morphologies (ESI, Fig. S1(a)–(c)†), the surface fluctuation is found to be less than 1 nm, as shown by the line profiles along the surface of the substrates (Fig. S1(d)–(f)†). It means that the processed $SrTiO_3$ (111) substrates are extremely smooth, which is essential for the growth of high quality Bi_2Se_3 .

The surface morphology of the synthesized Bi_2Se_3 thin film is also sensitive to the growth conditions, specifically the substrate temperature and growth time in our experiments. For instance, Bi_2Se_3 thin films displayed in large-scale AFM images (Fig. 1(a)–(c)) are prepared at 150 °C for 40 minutes, 190 °C for 60 minutes, and 190 °C for 90 minutes, respectively. The corresponding zoom-in zones with higher resolution (Fig. 1(d)–(f)) clearly demonstrate that nanometer-sized quasi-equilateral triangular terraces always exist, but the size and density of such terraces are distinctly different under these experimental conditions. Such a distinction is the starting point for our further study.

To quantitatively describe the surface morphology of the asprepared Bi₂Se₃ sample, the density, size, and height of triangular terraces are selected as three descriptors for the surface morphology. To avoid the statistical error, three 5 \times $5 \ \mu m^2$ patches at different positions of the same sample were chosen to confirm the homogeneity of the sample surface using AFM. Then in each $5 \times 5 \ \mu m^2$ area, we carefully scanned a $1 \times 1 \ \mu m^2$ spot at a random position. The average number of terraces in all the scanned spots was statistically counted to evaluate the average density of terraces. Meanwhile, the average side length of the quasi-equilateral triangle terraces was also recorded to characterize the size of surface domains. For example, the density and size of terraces for the sample in Fig. 1(b) are ~16 μ m⁻² and ~0.207 μ m, respectively. By measuring the line profiles along the surface, we can also obtain the height of triangular terraces, as shown in Fig. 1(g)-(i). Unlike the densities and sizes, which greatly vary at different temperatures and growth periods, most valleys between the character-



Fig. 1 Large scale AFM images of Bi₂Se₃ thin films grown on the SrTiO₃ (111) substrate. (a) AFM image of the Bi₂Se₃ film prepared at 150 °C for 40 minutes with the scale of 5 × 5 μ m². (b) AFM image of the Bi₂Se₃ film prepared at 190 °C for 60 minutes with the scale of 5 × 5 μ m². (c) AFM image of the Bi₂Se₃ film prepared at 190 °C for 90 minutes with the scale of 5 × 5 μ m². (c) AFM image of the Bi₂Se₃ film prepared at 190 °C for 90 minutes with the scale of 5 × 5 μ m². The white dashed squares marked in upper row are the lower row images, respectively. The red triangles marked in the lower row indicate the terrace average size with 137 nm, 210 nm and 376 nm, respectively. (g)–(i) The line profiles along the white lines in (d)–(f), respectively.

istic triangle-shaped terraces were found to adopt a uniform depth of ~ 3 nm for all the Bi₂Se₃ samples, corresponding to the height of three quintuple layers (QLs). The homogeneous height distribution of terraces may be attributed to the balance between island-like and layer-like growth of Bi2Se3 on SrTiO₃. In addition, the fluctuation in surface roughness is found to be comparable to the SrTiO₃ substrate for all samples, indicating that a very high quality of Bi₂Se₃ film is obtained in our experiment. It is noted that the RMS roughness measured in different sized areas was also measured to check the dependence of the scan area, as shown in Fig. S3, ESI.† We have collected the measured RMS value from different areas $(1 \times 1 \ \mu m^2, 2 \times 2 \ \mu m^2, 3 \times 3 \ \mu m^2)$. The plots are very close, and the minimum of RMS roughness is at the same temperature, indicating that our measured RMS roughness is reasonable.

Combining the information on the density, size, and height of Bi₂Se₃ terrace islands, we can define the surface roughness of the grown TI film, which connects the surface morphology and the classical wetting models. It is noted that there is also another kind of "roughness", named RMS roughness R_{RMS}, recorded by AFM measurement, as mentioned in the Introduction. As shown in Fig. S2(b),[†] the R_{RMS} is calculated merely based on the root-mean-square of the height for each pixel in the AFM image, which is generally used to roughly characterize the quality of the surface under study. However, such $R_{\rm RMS}$ cannot correctly reflect the relationship between the density and size of terraces on the Bi2Se3 surface, where the film with low-density and large-area terraces can adopt the same $R_{\rm RMS}$ as the surface with highly dense, small pieces of terraces. Therefore, we define the ratio of the total superficial area to the projected area as a more reasonable measure for the surface "roughness", named superficial area roughness R_{SA}, to distinguish such two Bi₂Se₃ surfaces with apparent different morphologies. As shown in the schematic diagram of the Bi_2Se_3 surface (Fig. 2(c)), the Bi_2Se_3 islands on the surface can be approximately treated as equilateral triangular prisms. R_{SA} can be calculated as

$$R_{\rm SA} = \frac{A_{\rm Total}}{A_0} = \frac{A_0 + A_{\rm Side}}{A_0} = 1 + \frac{A_{\rm Side}}{A_0} = 1 + \frac{3nLH}{A_0}, \qquad (1)$$

where *n* and *L* are the density and average side length of the triangular terraces, respectively, *H* is the height of the terrace determined by AFM, A_{Total} is the total superficial area, A_{Side} is the side area of the terraces, and A_0 is the projected area.

According to our experiments, both R_{RMS} and R_{SA} of the synthesized Bi₂Se₃ surface exhibit a non-monotonic relationship with the substrate temperature during growth, as shown in Fig. 2(a) and (b). The AFM measurements on the sample at various temperatures are shown in Fig. S4, ESI.[†] Such a nonmonotonic relationship demonstrates that increasing the substrate temperature appropriately can enhance the mobility of Bi and Se atoms, and accordingly inhibit the islandlike growth, leading to better film forming properties and smoother surface. However, if the growth temperature is too high, the films would be slowly destroyed by thermal



Fig. 2 RMS surface roughness (a) and superficial area roughness (b) of Bi₂Se₃ films grown at various substrate temperatures. (c) The schematic diagram of Bi₂Se₃ thin films grown on the SrTiO₃ (111) substrate. The red solid lines are linear fit.

disturbance, with small holes burnt through them, resulting in the increasing of roughness. Such kinds of small holes have a very small area, and thereby cannot appear in the $R_{\rm RMS}$ values. However, the superficial area is significantly increased due to the formation of these holes, reflected by the raised $R_{\rm SA}$. As a result, it is notable that the temperature for minimum $R_{\rm SA}$ (~190 °C) is 40 °C lower than the temperature for minimum $R_{\rm RMS}$ (~230 °C). As shown in Fig. S5,† the surface quality of the Bi₂Se₃ film prepared at 190 °C is quite high with large-sized regular triangle terraces. On the contrary, the surface of the film synthesized at 230 °C (the minimum in the $R_{\rm RMS}$ plot) displays higher dense small-sized terraces. It is clearly shown that the $R_{\rm SA}$ is a more reasonable index for characterizing the quality of vdW-layered materials with topographical surfaces.

3.2 Wetting of Bi₂Se₃ thin films

The wetting of the solid surface is usually characterized by CA θ , which obeys Young's equation

$$\gamma_{\rm s} = \gamma_{\rm sl} + \gamma_{\rm l} \cdot \cos \theta, \qquad (2)$$

where γ_s , γ_{sl} , and γ_l denote the energies of the solid surface, solid–liquid interface, and liquid surface, respectively. On the basis of Young's equation for an ideal surface, two classical wetting models were developed for the description of wetting on realistic surfaces: the Wenzel model in the case of the liquid in intimate contact with a micro-structured surface,^{29,30} as well as the non-wetting Cassie–Baxter (CB) model when the liquid is suspended on the top of microstructures.³¹ In the Wenzel model, the energy of the solid surface is proportional to its superficial area. Assuming that the terraced surface of the Bi₂Se₃ film is homogeneous in chemical composition, the Wenzel CA θ_W can be connected to the previously discussed superficial area roughness R_{SA} , in the expression of

$$\cos \theta_{\rm W} = R_{\rm SA} \cdot \cos \theta = \left(1 + \frac{3nLH}{A_0}\right) \cdot \cos \theta. \tag{3}$$

On the other hand, in the CB model for water on the rough Bi_2Se_3 surface, the liquid is only coming in contact with the top area of the triangular terraces, leaving tremendous air pockets at the inter-terrace valleys. Therefore, the surface energy is proportional to the area fraction of terraces *F*, and the CB contact angle θ_{CB} can be expressed as

$$\cos \theta_{\rm CB} = F \cdot (\cos \theta + 1) - 1 = \frac{\frac{\sqrt{3}}{4}nL^2}{A_0} \cdot (\cos \theta + 1) - 1. \quad (4)$$

It is noted that the thickness of the thinnest Bi_2Se_3 film in our experiment is ~8 nm, which can sufficiently screen the long-range electrostatic interaction from the underlying SrTiO₃ substrate. Therefore, the wettability of the Bi_2Se_3 thin film is identical to bulk, and the thickness of the Bi_2Se_3 films would play an irrelevant role in surface wettability.

To reveal which wetting state occurs to the Bi₂Se₃ surface with triangular terraces, we draw the relationship of the cosine value of the observed CA, $\cos \theta^*$, and R_{SA} in Fig. 3(a), and the relationship of $\cos \theta^*$ and F in Fig. 3(b), respectively. As shown in Fig. 3(a), $\cos \theta^*$ and R_{SA} exhibit a perfect linear relationship. However, the unexpected large slope (~17.5) and the non-zero intercept of the linear relationship demonstrate that the wetting of the terraced Bi₂Se₃ surface does not fit in with the conventional Wenzel model. On the contrary, $\cos \theta^*$ and Fdisplay an apparently nonlinear relationship, indicating that the wetting of Bi₂Se₃ is far from the Cassie state.

We perform further analysis to understand the unconventional Wenzel wetting state. Wettability is a function of the specific free energy which depends on its surface characteristics for any given surface. According to the measured surface topography, the surface energy of the terraced Bi₂Se₃ surface consists of two major parts: the energy of the topmost smooth Bi₂Se₃ surface and the energy of the edge-terminated side facets of triangular terraces. The surface energy of the edgeterminated side facet is considerably higher than that of the ideal smooth Bi₂Se₃ surface, due to the dangling bonds of unsaturated Bi and Se atoms and/or topological electronic states at the edge of terraces. By assuming that the free energy difference with and without water ($\gamma_s - \gamma_{sl}$) for the side surface



Fig. 3 The variation of water contact angle with superficial area roughness (a) and area fraction of terraces (b). The cases for the water droplet on the Bi_2Se_3 thin films with the smallest and largest contact angles are shown in (c) and (d), respectively. The black solid lines are linear fit.

is k times that for the ideal $\mathrm{Bi}_2\mathrm{Se}_3$ surface, eqn (3) can be revised as

$$\cos \theta_{\rm W} = \left(1 + k \cdot \frac{3nLH}{A_0}\right) \cdot \cos \theta$$
$$= (k \cdot \cos \theta) \cdot R_{\rm SA} + \cos \theta \cdot (1 - k). \tag{5}$$

In such a modified Wenzel model, $\cos \theta_{W}$ still adopts a linear relationship with R_{SA} , but the slope increases by k times, and the intercept becomes $\cos \theta^*(1 - k)$. The extrapolated CA of the ideal Bi₂Se₃ surface (the θ at $R_{SA} = 1$) is ~98.4°, indicating that the intrinsic Bi₂Se₃ is quite hydrophobic. On the other hand, the large value of $k (\sim -120)$ shows that the side facet of the terraces is extremely hydrophilic, where the unsaturated Se and Bi atoms are highly active to form chemical bonding with water. This is also the main reason why terraced surfaces adopt the Wenzel wetting state, although the intrinsic Bi₂Se₃ surface is hydrophobic. Another factor for Wenzel wetting of the Bi₂Se₃ surface is that the height of the terrace is too small, compared to the size of the terrace. Pioneering molecular dynamics simulations illustrate that the critical size for the existence of the Wenzel state on a pillared graphite surface is that when the pillar height is almost equal to the spacing between pillars.³² However, on the terraced surface of Bi₂Se₃ thin films, the height is only $\sim 1/100$ of the spacing between terraces (Fig. 1(g)-(i)), which is far below the threshold for the transition from the Wenzel state to the Cassie-Baxter state.

The high hydrophobicity makes the Bi2Se3 material very inert towards water, consistent with that reported by Yashina et al.33 This fact may also help to explain the robustness of the topological surface bands of Bi₂Se₃ under ambient conditions against air and moisture.34 Similar hydrophobic properties have also been reported on rare-earth oxides (CA = ~102°), as rare-earth metals have very weak interaction with oxygen in water, due to the screening of the outer shell to the inner 4f orbitals.^{35,36} In that case, water coming in contact with the surface forms a hydrophobic hydration structure, with one OH group in each water molecule perpendicularly pointing towards the surface.35 It is believed such a hydrophobic hydration structure also exists on the ideal Bi₂Se₃ surface, whose topmost layer is composed by Se atoms, and the Bi atoms are in the sub-layer, far from coming in contact with water molecules, leading to a very weak interaction with oxygen atoms in water. In addition, for water wetting on fluorocarbons, it was found that the "fatness" of the fluorine atom causes higher hydrophobicity of fluorocarbons than hydrocarbons.³⁷ Similarly, the longer lattice constant of (Bi₂Se₃: 4.16 Å; MoS₂: 3.16 Å), as well as the larger van der Waals radius (Se: 1.90 Å; S: 1.80 Å), also significantly decrease the surface energy of Bi₂Se₃, making its intrinsic wettability weaker than that of the MoS₂ film (CA = $\sim 90.4^{\circ}$).⁷ On the other hand, the edgeterminated steps and terraces of Bi₂Se₃ are extremely hydrophilic. As shown in Fig. 3(a), only 1% superficial area roughness can change the Bi₂Se₃ thin film from hydrophobic to hydrophilic. Therefore, under most experimental conditions, the Bi₂Se₃ surface with the presence of terrace edges could be hydrophilic. Furthermore, the wettability can be easily regulated by increasing or removing the surface topography, which is of great importance for Bi_2Se_3 applications.

To unveil the nature for the drastic difference in water affinity to the Se-terminated perfect surface and the Bi-exposed stepped edge of Bi₂Se₃ films, we perform first principles calculations on the water-Bi₂Se₃ interaction. The calculated binding energy between water and the stepped edge (0.49 eV) is ~ 5 times that on the perfect surface (0.11 eV). The calculated binding energies qualitatively display that the interaction between water and perfect Bi₂Se₃ (0.1 eV) is in the range of vdW interaction, while the much higher binding energy (0.5 eV) shows that the adsorption of water on the stepped edge is as strong as the chemical bonding interaction. As shown in Fig. 4(a), the adsorption configuration for water molecules with one OH vector pointing towards the topmost Se is confirmed, consistent with the wetting structure of rare-earth oxides.³⁵ While on the stepped edge (Fig. 4(b)), a flat-lying conformation of water molecule is obtained, where the O and H atoms are synchronously binding to exposed Bi and two Se atoms, respectively. The difference between the Bi-O distance (2.73 Å) and the sum of their van der Waals radii (3.59 Å) is much more significant than it is between the Se-H distance (2.63 Å) and the sum of their van der Waals radii (3.0 Å), indicating that the binding between water and Bi is much stronger than that between water and Se. Such a stronger interaction also modifies the electronic structure of adsorbed water. As demonstrated in Fig. 4(c-e), the projected density of states (pDOS) shows that the electronic structure of water adsorbed on the perfect Bi₂Se₃ surface is almost identical to the gas phase monomer. However, the highest occupied 1b1 orbital is



Fig. 4 The optimized geometries and isosurfaces of the difference electron density upon adsorption of single water on (a) perfect surface and (b) stepped edge of Bi₂Se₃, respectively. Atomic color code: O, red; H, white; Bi, purple; Se, yellow. The blue and yellow contours denote the increase and decrease of electron density of 0.001e per Å³. Density of states is also shown for (c) isolated water molecule, as well as for water adsorbed on (d) perfect surface and (e) stepped edge of Bi₂Se₃, respectively. The red area corresponds to the projected DOS to water, and the green area is attributed to the projected DOS to Bi₂Se₃.

greatly broadened for water coming in contact with the stepped edge site, indicating that the lone pair p electrons of oxygen are strongly doped into the empty d orbital of the exposed Bi atom. As displayed by the difference electron density plots in Fig. 4(a) and (b), the charge redistribution takes place upon water adsorption, where the electron density around surface Bi and Se is increased and decreased, respectively.

4. Conclusions

Our work provides detailed information on the water wettability of model topological insulator Bi2Se3 films. We demonstrate that the superficial area roughness R_{SA} is more suitable for characterizing the topography of real surfaces of Bi₂Se₃ thin films. Water contact angles of Bi₂Se₃ films show a linear increase when the relative surface roughness decreases, in excellent agreement with a modified Wenzel model. This model is based on the chemical nature that the perfect surface of vdW-layered materials is inert, but the edge, where dangling bonds exposed, is much more affinitive to water. It may be generatively suitable for vdW-layered materials with terraced surfaces. Thus, by measuring CA, we can quickly measure the surface roughness, which can roughly characterize the quality of the synthesized Bi₂Se₃ sample without tedious and costly AFM measurement. In addition, the water contact angle of the ideal smooth Bi_2Se_3 surface is inferred to be ~98.4°, indicating that it is intrinsically hydrophobic, which can explain the previously reported inertia of Bi₂Se₃ to water. In sharp contrast, the side facet or the edge of the Bi₂Se₃ terrace is extremely hydrophilic, which can be used for the regulation of the wettability of the Bi₂Se₃ surface. Similarly, it is also understandable why the wettability of the layered material such as graphene significantly varies in several reports,^{5,6,11} since a tiny difference in the amount of side facets or defects can lead to hydrophobic/hydrophilic transition. The hydrophobic nature of Bi₂Se₃ is highly beneficial for protecting its metallic surface states and for its practical uses in Bi2Se3-based microelectronic and spintronic devices.

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