CRYSTAL GROWTH & DESIGN

ARTICLE

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Formation of Inert Bi_2Se_3(0001) Cleaved Surface

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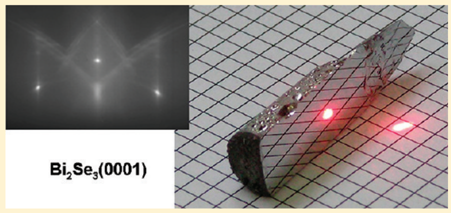
S *Supporting Information*

ABSTRACT: A high quality inclusion-free Bi_2Se_3 crystal has been grown by the Bridgman method with the use of a rotating heat field. A large-area atomically flat Bi_2Se_3(0001) surface of excellent crystallographic quality has been formed by cleavage. Chemical and microstructural properties of the surface have been evaluated with reflection high-energy electron diffraction, atomic force microscopy (AFM), scanning tunneling microscopy (STM), spectroscopic ellipsometry, and X-ray photoelectron spectroscopy. There was no Bi_2Se_3(0001) surface oxidation detected after over a month in air under ambient conditions as shown by comparative core level spectroscopy, AFM, and STM.



INTRODUCTION

Bismuth selenide, Bi_2Se_3, is a compound well-known for its pronounced layered crystal structure and good thermoelectric properties.[1−3] In recent years, the crystal has attracted great attention as a three-dimensional topological insulator (TI).[4−9] This new electronic system is characterized by a combination of an insulating bulk and conducting surface states of massless Dirac fermions. Several methods have been proposed for the experimental realization of such electronic states at the crystalline surface of Bi_2Se_3. Epitaxial thin films and nanocrystals can be used for an observation of the TI surface electronic effects.[6,10−14] Because of good cleavage properties of Bi_2Se_3 crystal, the (0001) surface can be prepared by mechanical cleaving of the bulk crystal, and this method was also used in several experiments on the TI effect observation but without a clear description of crystal growth conditions and surface preparation.[7,9,15−18] The formation and stability of TI state at the crystal−vacuum (or crystal −air) boundary, however, may be strongly dependent on the structural and chemical quality of Bi_2Se_3 crystal, and the top surface properties seem to be among the governing factors.

Generally, it is known that halcogenide compounds tend to oxidize in air due to their drastic affinity with oxygen.[19−24] For many complex halcogenide compounds, the chemical interaction with air agents results in complete decomposition and amorphization with time that limits the crystal living period. From this common point of view, the Bi_2Se_3 crystal appears to be not an exception, and, respectively, oxide presence could be expected at the crystal surface. Indeed, oxygen signal was detected by X-ray photoelectron spectroscopy in several studies devoted to a complex evaluation of the Bi_2Se_3 nanocrystals prepared by hydrothermal reactions.[25−27] The behavior of cleaved Bi_2Se_3(0001) surface is less clear. On the one hand, there are reports on swift oxidation of Bi_2Se_3(0001) surface in air at ambient and increased temperatures.[28,29] On the other hand, layered halcogenide crystals generally display a pronounced chemical inertness of the cleaved surface. For example, the cleaved Se-terminated optical-quality surface of GaSe crystal is long-living in air and widely applied in nonlinear optical devices.[30]

The crystal structure of trigonal Bi_2Se_3, space group $R\bar{3}m$, is shown in Figure 1.[31,32] The crystal lattice of this modification is formed by bilayers of face-sharing $BiSe_6$ octahedrons (quintuple). The bilayers are stacked along the *c* axis by weak van der Waals bonds with a Se−Se distance as long as 351 pm. On cleavage these long Se−Se bonds are disrupted, and after relaxation the

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