Inertness and degradation of (0001) surface of Bi_2Se_3 topological insulator

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Inertness of the cleaved (0001) surface of the Bi_2Se_3 single crystal, grown by modified Bridgman method, to oxidation has been demonstrated by X-ray photoelectron spectroscopy, scanning tunneling microscopy, and by *ab initio* DFT calculations. No intrinsic bismuth and selenium oxides are formed on the low-defect, atomically flat $Bi_2Se_3(0001)$-(1×1) surface after a long-time air exposure. The inertness of $Bi_2Se_3(0001)$ to O_2 and NO_2, as well as bismuth-oxygen bonding formation under molecular adsorption in the Se vacancy was supported by DFT calculations. [http://dx.doi.org/10.1063/1.4767458]

I. INTRODUCTION

In recent years, extensive studies of V-VI compounds including Bi_2Se_3 and Bi_2Te_3 have been made in order to develop efficient materials for higher performance devices based on high speed and spin-polarized carriers with light effective mass.[1] However, for these materials, various problems arise which hinder a prompt practical realization of mass-producible devices. It was shown that the surface electronic properties of the three-dimensional topological insulators (TIs) were affected by the surface adsorption of residual gases,[2] air,[3] CO,[4] H_2O,[5] and oxygen.[7,8] In particular, the air exposure over several hours apparently causes the surface oxidation and environmental doping.[6–8] It was demonstrated that oxidation of Bi_2Se_3 results in a complex band structure because of hybridization of the O-derived states with the substrate states.[9] The formation of intrinsic oxides observed on the (0001) Bi_2Se_3 and Bi_2Te_3 surfaces can be responsible for the change of sign in surface conductivity with time[10] and even for deterioration of the topological surface states properties[7] as well as for reduction of the spin current.[9]

On the other hand, the stability and atomic flatness of the surfaces cleaved across weak interlayer bonds in layered structure materials, such as graphite and the transition metal dichalcogenides are well known.[11] From the theoretical point of view, one can expect that the (0001) $Bi_2Se(Te)_3$ surfaces should be also stable to oxidation, which is in contradiction with recent results of Refs. 7 and 8. Unfortunately, no detailed analysis of the structural perfection of the studied surfaces was given in Refs. 7 and 8. It is well-known that inertness to oxidation depends on the amount of surface defects (vacancies, substitutional defects, and steps).[12] One can expect that the perfect (0001) V–VI surfaces with low-density of surface defects concentration should be inert to oxidation because the (0001) surface is stabilized by Se(Te) atoms with covalent bonds oriented into a quintuple layer.

In this work, the properties of the (0001) surface of Bi_2Se_3 grown by the Bridgman method with the use of a rotating heat field were studied experimentally to find out a relation between the structural perfection, chemical stability, and TI properties of single-crystalline Bi_2Se_3. The inertness of $Bi_2Se_3(0001)$ to the oxidation is confirmed by DFT calculations.

II. METHODS

The Bi and Se of 99.999% purity were used for synthesis of polycrystalline Bi_2Se_3. Suspended components were sealed off in an ampoule which was pumped down to a residual pressure of $\sim 10^{-4}$ Torr. The ampoule was heated in an oven at the rate of $20\,^{\circ}C/h$ until the temperature became $20\,^{\circ}C$ higher than the melting point ($T_{melt} = 705\,^{\circ}C$). The oven was switched off in one day. Recrystallization of the obtained ingots was performed using the vertical variant of the Bridgman method with a rotating heat field.[13] The grown crystals consisted of one or several large single crystalline blocks, as shown in Fig. 1(a). As received, fresh surfaces are readily available by cleaving the crystals along its natural cleavage plane. We have found that the surface quality is very sensitive on the cleavage method, in particular, the cleaving with a scotch tape induces a lot of defects while splitting by a cleaver provides nearly a perfect surface. The defects like a half-height quintuple layer induced by scotch cleaved were found in Ref. 14.

The AFM image of the perfectly cleaved surface is shown in Fig. 1(b). The height profile (peak to peak) along the line shown in Fig. 1(b) is given in Fig. 1(d). One can see that the change in the height does not exceed 0.1 nm at 4 μm

