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Tracking quintuple layer oxidation on cleaved Bi$_2$Se$_3$ by optical second-harmonic anisotropy

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We find that the major and minor intensity lobes of a measured rotational-anisotropy pattern of optical second-harmonic generation (SHG) from a cleaved Bi$_2$Se$_3$ (111) surface can gradually change with time and eventually switch their relative amplitudes. This switching provides a means for tracking the progress of surface oxidation inside a quintuple layer of Bi$_2$Se$_3$. At different stages of oxidation, we perform pump-probe SHG experiments to study charge dynamics at the oxide/Bi$_2$Se$_3$ interface and to detect spin polarization of photoexcited surface states in the Bi$_2$Se$_3$ topological insulator.

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Topological insulators are bulk insulators with conducting surface states that are protected from backscattering by time-reversal symmetry [1]. These topological surface states behave like gapless Dirac fermions but have their spin locked perpendicular to their momentum [1–4], projecting important essential features have not been grasped. Studying the time-dependent behavior of SHG should elucidate the mechanism of surface oxidation, laser photoinjection, and undetermined and studying the effect can help resolve the convoluted effects of surface oxidation in the top few atomic layers of Bi$_2$Se$_3$, and studying the effect can help resolve the convoluted effects of surface oxidation, laser photoinjection, and undetermined crystal orientation. Furthermore, we perform pump-probe SHG measurements to study the charge dynamics and spin polarization of photoexcited surface states, comparatively on freshly cleaved and oxidized Bi$_2$Se$_3$ surfaces.

Measurements of SHG were performed in reflection from cleaved (111) surfaces of an undoped Bi$_2$Se$_3$ single crystal. The surfaces were cleaved via scotch tape exfoliation in air. A dry N$_2$ jet from a gas nozzle was projected directly toward the surface to dissipate heat produced by the laser. The laser was a Ti:Sa oscillator at a wavelength of 740 nm with a pulse duration of $\sim 120$ fs and a repetition rate of 82 MHz. The laser beam was chopped at 3.3 kHz to further reduce laser heating. The probe beam for SHG at a 45° incident angle was focused to a 30-μm spot on the sample, resulting in a fluence of $\sim 35 \mu J/cm^2$. The SH light was detected by a photomultiplier tube. For pump-probe SHG, a time-delayed pump beam was spatially overlapped to the probe beam on the sample. The pump beam at a 30° incident angle was focused to a 75-μm spot, resulting in a fluence of $\sim 11 \mu J/cm^2$.

The experimental geometry, including the pump, probe, SHG beams and the lattice structure, is schematically shown in Fig. 1. Complementary x-ray photoelectron spectroscopy (XPS) measurements were performed using a Al Kα beam at 1487 eV, focused to a 400-μm spot on the sample.

RA-SH patterns from the Bi$_2$Se$_3$(111) surface can be predicted from symmetry analysis of the second-order
FIG. 1. Schematic of the pump-probe SHG beam geometry, the coordinate x and y axes, and the atomic-layer structure in a Se-Bi-Se quintuple layer. At azimuthal angle $\phi = 0^\circ$, the y axis is perpendicular to the mirror plane of symmetry, and importantly, the incident laser beam faces toward the x axis.

susceptibility tensor $\chi_{ijk}^{(2)}$. The Bi$_2$Se$_3$ crystal is a layered structure composed of quintuple layers (QLs) [4], whereas each QL is itself a layered structure of five hexagonal lattices following the sequence of Se-Bi-Se-Bi-Se atomic layers as shown in Fig. 1. SHG is forbidden from a free-standing QL because of its inversion symmetry. For a Bi$_2$Se$_3$ crystal, three QLs are needed to form a lattice section that can accommodate a unit cell, whereas each QL is an inversion image of its neighboring QL. Therefore, SHG is forbidden in the bulk of Bi$_2$Se$_3$, and the only possible source of SHG is at the surface where inversion symmetry is broken. Because the surface structure has $C_{3v}$ symmetry, $\chi_{ijk}^{(2)}$ at the surface can be simplified to have only four nonzero independent elements $\chi_{zzz}$, $\chi_{zxx}$, $\chi_{xxx}$, and $\chi_{xxx}$. The corresponding coordinate system is defined such that the y axis is perpendicular to the mirror plane of symmetry and the x axis points in the direction as shown in Fig. 1, determined by our x-ray diffraction measurements [27].

For a $p$-polarized incident beam at frequency $\omega$ and a $p$-polarized analyzing SH beam at frequency $2\omega$, the RA-SH intensity from the Bi$_2$Se$_3$(111) surface can be written as [8,26]

$$I^{(2\omega)}(\phi) = |a_0 + a_3 \cos (3\phi)|^2,$$

(1)

where $\phi$ is the sample azimuthal angle between the incident plane and the x axis in Fig. 1. Here $a_0$ and $a_3$ are the isotropic and anisotropic coefficients, respectively, and can be expressed as

$$a_0 = c_0 \chi_{zzz} + c_2 \chi_{zxx} + c_3 \chi_{xxx}, \quad a_3 = c_3 \chi_{xxx},$$

(2)

where $c_0$ and $c_3$ are constants determined by dielectric functions and $\chi_{zzz}$, $\chi_{zxx}$, $\chi_{xxx}$, and $\chi_{xxx}$ are the susceptibility elements in the coordinate system of Fig 1. If $a_3$ is chosen to be real and positive, then $a_0$ will be complex, having a real part $a_0^r$ and an imaginary part $a_0^i$, i.e., $a_0 = a_0^r + ia_0^i$. The RA-SH pattern in Eq. (1) is threefold symmetric when $a_0^i \neq 0$, having three major lobes alternated by three minor lobes. The $\phi = 0^\circ$, $120^\circ$, and $240^\circ$ angles are equivalent, and the $\phi = 60^\circ$, $180^\circ$,
and 300° angles are equivalent; therefore, only two crystal directions are independent in a RA-SH scan. The major lobe is at either $\phi = 0°$ or $180°$ but not specified, and this means an ambiguity of the ± principal crystal direction ($x$ axis) in a QL, which has not been solved previously [8–11].

Figure 2(a) shows the measured RA-SH scans from the Bi$_2$Se$_3$ surface immediately, and at 1, 2, 6, 12, and 24 h after sample cleavage, and each scan was taken at a different sample spot but on the same single-crystal domain to avoid prior laser exposure before each measurement. Figure 2(b) shows the measured RA-SH scans immediately and at 0.5, 1, 1.5, 2, and 3 h after sample cleavage, and all these scans were taken at the same sample spot under continuous laser irradiation after cleavage. In both cases, the RA-SH scans vary similarly in shape but differently in amplitude and rate of change. The major lobe at $\phi = 180°$ gradually shrinks as the minor lobe at $\phi = 0°$ grows, and eventually, all major and minor lobes turn into each other. The remarkable sixfold RA-SH appears at a critical time when $\alpha_0 = 0°$. Figure 2 shows that continuous laser irradiation shortens this critical time from 6 to 1 h.

To associate the RA-SH results with oxidation, we performed XPS measurements to study the time-dependent chemical composition at the Bi$_2$Se$_3$ surface. Figure 3(a) shows the XPS spectra near the Bi 5$d_{3/2}$ and 5$d_{5/2}$ binding energies measured immediately $t = 0$ and at $t = 3$ h and $t = 8$ h after Bi$_2$Se$_3$ sample cleavage. The spectra are vertically offset by 2000 counts for clarity. As indicated by the vertical arrows, the Bi$_2$O$_3$ oxide peaks appear at $t = 3$ h and grow larger at $t = 8$ h. (b) Schematic of the upper and lower half quintuple layers. The arrows indicate the effective dc electric field for FI-SH.

As the upper HQL is partially oxidized, the oxide/Bi$_2$Se$_3$ interface moves downward, and the effective dc electric field $E_1$ (as indicated by the arrows) because of symmetry breaking for FI-SH varies accordingly. We divide the total SH field into three components: FI-SH because of symmetry breaking, FI-SH because of charge photoinjection across the oxide/Bi$_2$Se$_3$ interface, and SHG from the partially oxidized QL, and then the time-dependent RA-SH intensity can be written as

$$I^{(2\omega)}(\phi,t) = \left[ \left( \frac{1 + t}{t_1} \right) \left[ a_0^{E_1} + a_3^{E_1} \cos(3\phi) \right] - (1 - e^{-t/t_2}) \left[ a_0^{E_2} + a_3^{E_2} \cos(3\phi) \right] - \frac{t}{t_0} \left[ a_0^{HQL} + a_3^{HQL} \cos(3\phi) \right] \right]^2. \quad (3)$$

Here $t$ is the time lapse after sample cleavage, $t_1$ and $t_2$ and $t_0$ are the time constants of their respective SH fields, $a_0^{E_1}$ and $a_3^{E_1}$ are the RA-SH coefficients from the symmetry-breaking field $E_1$, $a_0^{E_2}$ and $a_3^{E_2}$ are the RA-SH coefficients from the photoinjection field $E_2$, and $a_0^{E_1}$ and $a_3^{E_1}$ are the RA-SH coefficients of the upper HQL. The third term in Eq. (3) is derived from two SH fields: one from the partially oxidized upper HQL and the other from the unoxidized lower HQL. They cancel each other when $t = 0$ because of inversion symmetry. When $t = t_0$, the upper HQL is fully oxidized and thus does not produce SHG. When $t < t_0$, the SH field from the upper HQL presumably varies as $(1 - t/t_0)$ because oxidation reduces the volume for SHG, whereas that from the lower HQL stays constant. The second term in Eq. (3) is negligible for the RA-SH scans in Fig. 2(a) because photoinjection is negligible but becomes important for the RA-SH scans in Fig. 2(b). The variation of both the FI-SH and the oxide/Bi$_2$Se$_3$ interface position results in a relative change in $\alpha_0$ and $\alpha$ and thus a major-to-minor lobe switching. We can reasonably assume that a sixfold RA-SH corresponds to the time when a half of a QL is oxidized, and a full major-to-minor lobe switching corresponds to the time when a full QL is oxidized. Based on this assumption and using Fig. 2(a), we obtain $t_0 = 6$. The time for oxidation of a half QL can be further estimated as 3 h because RA-SH varies mostly during this time. The RA-SH shows a gradual evolution of oxidation within a QL during the 12-h period, whereas the XPS spectra do not reveal the gradual nature when $t < 3$ h. When $t > t_0$, Eq. (3) is not valid anymore because oxidation becomes slower [14] and SHG from the second QL should be considered. As the oxidation goes through multiple QLs, periodic lobe switching is expected, but this has not been observed in our measurements.

At different stages of oxidation, we also perform pump-probe SHG measurements [10,29] on cleaved Bi$_2$Se$_3$, mainly to detect spin polarization of the surface states following photoexcitation by a circularly polarized pump. This also gives charge dynamics at the oxide/Bi$_2$Se$_3$ interface. Figure 4(a) shows the measured SH signal as a function of the pump-probe delay time $\Delta t$ from an oxidized Bi$_2$Se$_3$(111) surface, which had been exposed to air for 48 h after cleavage, at the fixed azimuthal angle $\phi = 60°$. The pump in Fig. 4(a) is right-hand circularly (RC) polarized, but a left-hand circularly (LC) polarized pump yields almost the same result (data not

FIG. 3. (a) XPS spectra near the Bi 5$d_{3/2}$ and 5$d_{5/2}$ binding energies measured immediately $t = 0$ and at $t = 3$ h and $t = 8$ h after Bi$_2$Se$_3$ sample cleavage. The spectra are vertically offset by 2000 counts for clarity. As indicated by the vertical arrows, the Bi$_2$O$_3$ oxide peaks appear at $t = 3$ h and grow larger at $t = 8$ h. (b) Schematic of the upper and lower half quintuple layers. The arrows indicate the effective dc electric field for FI-SH.
The SH signal drops about 15% to a minimum when the delay time is at $\Delta t = 0.13$ ps.

Figures 4(b) and 4(c) show the measured RA-SH scans from the oxidized Bi$_2$Se$_3$ surface and a freshly cleaved surface, respectively. Each panel also includes two RA-SH scans when there is a RC or LC pump at the delay time of $\Delta t = 0.13$ ps. For the oxidized surface, we first saturated the RA-SH scans with continuous irradiation of both the pump and probe to avoid the time-dependent SHG during each RA-SH measurement. Figure 4(b) shows that the pump-induced change is an $\sim 20\%$ drop at $\phi = 0^\circ$ but negligible at $\phi = 180^\circ$, similar for both RC and LC pumps. No apparent difference between the RC and the LC pumps suggests that pump-induced spin polarization is not observed by SHG for the oxidized sample. Actually, a $45^\circ$ linearly polarized pump produces almost the same pump-induced change in SHG (data not shown) as that in Fig. 4(b), and thus pump polarization is not critical for the drop of SHG. The large pump-induced change in SHG at $\phi = 0^\circ$ can be explained by a transient thermoelectric current [12,30] in the vertical direction, which arises from the thermal effect of the pump because of a large vertical temperature gradient. During the time of $\Delta t = 0.13$ ps, pump-excited surface states migrate into the Bi$_2$Se$_3$ bulk, creating a transient electric field that diminishes the dc electric field slowly built by photoinjection and this results in a reduced SH signal. Figure 4(c) shows that RC and LC pumps produce slightly different RA-SH scans in their fits, indicating a SH response of spin polarization of photoexcited surface states on the freshly cleaved surface. The pump-induced changes in SHG are an $\sim 30\%$ drop at $\phi = 0^\circ$ and an $\sim 22\%$ drop at $\phi = 180^\circ$, which can also be explained by the same vertical transient thermoelectric current. Different charge dynamics for the oxidized and freshly cleaved surfaces suggests that trapped charge in the oxide layer likely does not contribute to the transient thermoelectric current. Figures 4(b) and 4(c) show that the pump-induced change in SHG is also strongly anisotropic and can be used to track QL oxidation.

In comparison to these earlier results of SHG from Bi$_2$Se$_3$ surfaces [8–11], our results show that the major lobe of RA-SH can be at a $\phi = 0^\circ$ or $180^\circ$ crystal direction, depending on the measurement time since cleavage. These two directions have not been well defined previously and could be further confused by the unspecified amount of oxidation in previous results. Our pump-probe SHG signals in Fig. 4(a) show a similar magnitude of pump-induced change [10], but our noise level appears higher, easily overwhelming a subtle SH response of spin polarization. The noise level can be suppressed by averaging over a longer time, but it is not feasible to measure over an extensive time because there is a strong time dependence of SHG, either from charge photoinjection on oxidized surfaces or from rapid oxidation on freshly cleaved surfaces. To detect laser-injected spin polarization, further efforts are needed to develop a new pump-probe SHG technique that can almost simultaneously compare the SHG signals under RC and LC pumps.

To summarize, we have performed an experimental study of time-dependent RA-SH and pump-probe SHG from the cleaved Bi$_2$Se$_3$ surface as it undergoes oxidation. We find that the major and minor lobes of a RA-SH pattern can gradually switch their intensities over time, and this lobe switching not only can track the progress of oxidation inside a quintuple layer at the Bi$_2$Se$_3$ surface, but also can determine the polarity of principal crystal directions in Bi$_2$Se$_3$. Our pump-probe SHG results show that SHG may detect spin polarization of photoexcited surface states on Bi$_2$Se$_3$ surfaces when charge trapping due to laser photoinjection can be effectively suppressed. Our results can be generalized to a broad range of Bi$_2$Se$_3$-type layered materials, and should provide guidance for the development of ultrafast nonlinear optical techniques for probing surface-specific charge and spin dynamics in topological insulators.

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