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Nonlinear Optical Probe of Tunable Surface Electrons on a Topological Insulator

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We use ultrafast laser pulses to experimentally demonstrate that the second-order optical response of bulk single crystals of the topological insulator Bi2Se3 is sensitive to its surface electrons. By performing surface doping dependence measurements as a function of photon polarization and sample orientation we show that second harmonic generation can simultaneously probe both the surface crystalline structure and the surface charge of Bi2Se3. Furthermore, we find that second harmonic generation using circularly polarized photons reveals the time-reversal symmetry properties of the system and is surprisingly robust against surface charging, which makes it a promising tool for spectroscopic studies of topological surfaces and buried interfaces.

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where $A$ is a constant determined by the experimental geometry, $\hat{e}$ is the polarization of the incoming or outgoing photons, $I(0)$ is the intensity of the incident beam, and $X_{ijk}^{(2)}$ is a 27 component tensor. Application of $C_{3v}$ symmetry reduces $X_{ijk}^{(2)}$ to four nonzero independent components $X_{xxx} = -X_{xxy} = X_{xyy}, X_{xxz} = X_{xyz}, X_{xyz} = X_{xyz}$, and $X_{zzz}$. By controlling the relative orientation between the beam polarizations and crystal axes as shown in Fig. 1(a), components describing the in-plane and out-of-plane electrical responses can be isolated via

$$I_{PP}(2\omega) = A \times |a^{(3)} - 0.025a^{(1)}\cos(3\phi)|^2$$
$$I_{SP}(2\omega) = A \times |a^{(2)} + 0.016a^{(1)}\cos(3\phi)|^2$$
$$I_{PS}(2\omega) = A \times |0.020a^{(1)}\sin(3\phi)|^2$$
$$I_{SS}(2\omega) = A \times |0.013a^{(1)}\sin(3\phi)|^2$$

Figure 1 shows the dependence of SHG intensity from the (111) surface of Bi2Se3 measured under different polarization geometries. The experiments were performed in air at room temperature and data were taken both immediately after and 200 minutes after the sample was cleaved. The time dependence of the SHG patterns is related to surface charging as discussed later in the text. The SHG patterns exhibit a sixfold or threefold rotational symmetry depending on whether S- or P-polarized output photons are selected, respectively. Because S-polarized light only has in-plane electric-field components, it is only sensitive to the in-plane response $a^{(1)}$ likely originating from anharmonic polarizability of Se-Se bonds [Fig. 1(b)], which have a sixfold symmetric arrangement. On the other hand, because P-polarized light contains an electric-field component along $\hat{e}$, it is sensitive to out-of-plane responses $a^{(2)}$ and $a^{(3)}$ originating from the Se-Bi bonds, which have a threefold symmetric arrangement. A fit of Eq. (2) to the SHG patterns measured at a given time after cleavage using a single set of susceptibility tensor elements [21] yields excellent agreement [Figs. 1(c)–1(j)], which shows that the data are consistent with surface SHG from Bi2Se3.

To prove that the surface contribution to SHG is dominant, we study its response to changes in the surface carrier concentration. It is known from angle-resolved photoemission spectroscopy [22] that after cleavage the surface electron concentration of Bi$_2$Se$_3$ increases monotonically over an hour-long time scale before stabilizing. To study how this affects SHG we measure its time dependence immediately after cleavage. Figures 1(c)–1(j) show a clear change in the magnitude of all SHG patterns between $t = 0$ and $t = 200$ mins but no change in their rotational symmetry, which precludes a trigonal symmetry breaking reconstruction. To investigate the possibility of surface atomic displacements that preserve overall trigonal symmetry such as a change of interlayer distance, which would affect the in- and out-of-plane susceptibilities differently, we compare the complete time dependence of SHG intensities under different linear polarization geometries. Figure 2 shows that different combinations of susceptibility components all undergo the same monotonic increase by as much as 400% between $t = 0$ and $t = 50$ mins following cleavage, after which they saturate to a value that remains constant out to at least 600 mins, a trend that remains constant out to at least 600 mins, a trend.
highly consistent with the evolution of the surface Fermi level observed using angle-resolved photoemission spectroscopy [22]. To rule out photo-induced effects, we measured the time dependence without exposing the sample to light for the first 100 mins after cleavage. In this case we find that the SHG intensities remain constant at the pre-saturation values [insets, Figs. 2(c) and 2(d)], indicating that the initial rise in SHG intensity is purely a surface doping effect and not a photo-induced effect [23–25]. Such large percentage changes in SHG intensity with surface electron doping suggest that SHG comes predominantly from electrons at the surface.

Microscopically, the increased surface carrier concentration affects SHG intensity through the perpendicular surface electric field $\vec{E}$ that it creates. SHG is highly sensitive to a static electric field because it breaks inversion symmetry over the region that it penetrates, which is typically around 20 Å for metallic Bi$_2$Se$_3$ [26]. Electric-field-induced SHG is commonly observed in the context of metal-electrolyte interfaces, and is theoretically described by a third order process $P_i(2\omega) = \chi^{(3)}_{ijk}\vec{E}_j(0)\vec{E}_k(\omega)\hat{\epsilon}_i(\omega)$ [19,23] that acts in addition to $\chi^{(2)}$ in Eq. (2). Because $\chi^{(3)}$ has the same symmetry constraints as $\chi^{(2)}$ [21], the overall symmetry of the SHG patterns must remain unchanged in the presence of $\vec{E}$. To demonstrate that SHG is sensitive to tuning the surface Fermi level, we deposit O$_2$ on the surface, which has been shown to be an effective electron acceptor on Bi$_2$Se$_3$(111) [27]. Figure 3 shows the time dependence of $I_{pp}(2\omega)$ after cleaving in an O$_2$ environment. We find that the SHG intensity exhibits an initial fast upturn reaching about 50% of the saturation intensity value in air, followed by a gradual decrease back to its initial value. These results show that electron transfer from the Bi$_2$Se$_3$ surface to O$_2$ molecules takes place only after some finite $\vec{E}$ has developed, and that O$_2$ can restore the surface back to an uncharged ($\vec{E} = 0$) state but cannot hole dope beyond this state. These behaviors are consistent with $\vec{E}$ arising from the migration of negatively charged Se vacancies to the surface, which acts to lower the surface energy of the topmost Se layer. Assuming that charge transfer only takes place when an O$_2$ molecule is adsorbed at a surface Se vacancy site, no additional hole doping will occur once all vacancies are occupied. Such a mechanism naturally explains the slow time scale on which $\vec{E}$ develops, and why the same behavior is observed regardless of whether the sample is cleaved in air or in ultrahigh vacuum [22].

Having established an optical method to probe the spatial symmetry and Fermi level of Bi$_2$Se$_3$ surface electrons, we show how SHG can monitor time-reversal symmetry (TRS) at a topological insulator surface. It has been proposed that new TRS broken phases can be measured through the differential absorption of right (R) versus left (L) circularly polarized light [6,14,15]. However, it is known that the linear response of Bi$_2$Se$_3$ to circularly polarized light is only sensitive to bulk electrons [16]. To understand if second harmonic versions of such experiments are feasible, it is necessary to measure the intrinsic second-order surface response of Bi$_2$Se$_3$ to circularly-polarized light.

Second harmonic circular dichroism (CD), the difference in SHG yield using incident R- versus L-polarized fundamental light, was measured from Bi$_2$Se$_3$ 200 minutes after cleavage in air. Figures 4(a) and 4(b) show that the
The realization of surface SHG from Bi$_2$Se$_3$ and the demonstration of its sensitivity to the surface Fermi level, crystal symmetry, and TRS provides a novel contact-free probe of the properties of a single surface of a topological insulator. This could be used to probe the structural and electronic properties of buried topological insulator interfaces, and to search for exotic broken symmetry interface phases. Using ultrashort laser pulses also permits the study of time-resolved nonequilibrium dynamics of a surface or interface following an excitation, which could be applied to probe photo-induced spin-polarized currents.

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FIG. 4 (color). Normalized $\phi$-dependent SHG intensity patterns measured 200 minutes after cleavage in air under (a) left-circular in ($L_{in}$) $S_{out}$ and right-circular in ($R_{in}$) $S_{out}$, and (b) $L_{in}$-$P_{out}$ and $R_{in}$-$P_{out}$ photon polarization geometries. Solid lines are theoretical fits (see text). (c) Circular dichroism ($I_R-I_L$) corresponding to data in panels (a) and (b). (d) Difference between circular dichroism measured at 200 minutes after cleavage and immediately after cleavage.

SHG patterns obtained using $R$- and $L$-polarized incident light are clearly different for both $P$- and $S$-polarized output geometries, which are well described using Eq. (1) with the same set of susceptibility values fitted to Figs. 1(g)–1(j). Although higher multipole bulk contributions to SHG, which are allowed in inversion symmetric crystals, may contribute to CD due to an interference with the surface dipole radiation [19], such bulk terms are known to be greatly suppressed relative to surface dipolar terms in the regime where the photon energy exceeds the bulk band gap [28]. Our experiment is in this regime and we have experimentally shown that the surface contribution is indeed dominant [Figs. 1–3]. While CD is generally nonzero, Fig. 4(c) shows that it vanishes when $\phi$ is an integer multiple of 60°, angles where the scattering plane coincides with a mirror plane of the (111) surface. Such zeroes are protected by mirror symmetry because $R$- and $L$-polarized light transform into one another under mirror reflection about the scattering plane. Because a magnetization can break mirror symmetry, measuring departures from zero in CD along these specific values of $\phi$ can be a sensitive probe of TRS breaking on the surface of Bi$_2$Se$_3$.

Remarkably, we find that CD at a general $\phi$ is insensitive to surface charging, as evidenced by the lack of measurable change as a function of time after cleavage [Fig. 4(d)]. This suggests that sensitive searches for TRS breaking induced CD may be carried out without the need for careful control of surface charging, which is an important and robust way of studying the physics of surface doped topological insulators or buried interfaces between topological insulators and ordinary materials [1,2].

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