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# Raman and interband optical spectra of epitaxial layers of the topological insulators $\text{Bi}_2\text{Te}_3$ and $\text{Bi}_2\text{Se}_3$ on $\text{BaF}_2$ substrates

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## Abstract

We report results of Raman and ellipsometric spectroscopy of the topological insulators  $\text{Bi}_2\text{Te}_3$  and  $\text{Bi}_2\text{Se}_3$  grown by molecular beam epitaxy on  $\text{BaF}_2$  (111) substrates. Surfaces and interfaces of the films are probed by Raman scattering from the front and back sides of the samples, which is possible owing to the transparent substrate. Surface modifications induced by intense illumination with exciting laser light have been detected, with excess tellurium at the surface during and after exposure. We also report data for thin epilayers containing a fractional number of unit cells and/or incomplete  $\text{Bi}_2\text{Te}_3$  and  $\text{Bi}_2\text{Se}_3$  quintuples. We have used spectroellipsometric measurements to obtain response functions and have derived the penetration depth of light in the 1.0–6.5 eV range.

Keywords: bismuth tellurides, bismuth selenides, Raman spectra, ellipsometric spectra, epitaxial layers

## 1. Introduction

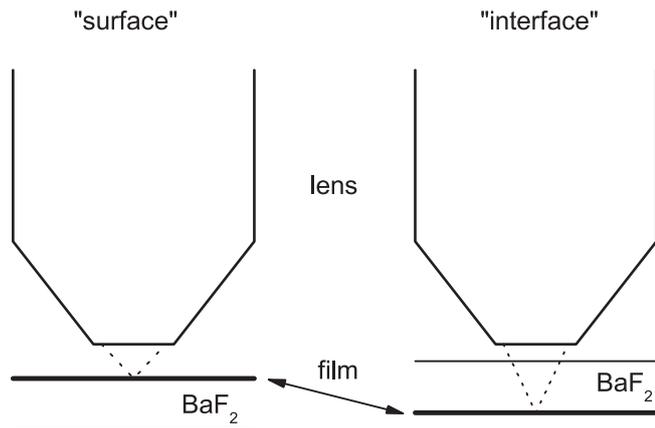
Topological insulators are currently attracting widespread attention mainly owing to their peculiar surface states [1]. The bismuth chalcogenides  $\text{Bi}_2\text{Te}_3$  and  $\text{Bi}_2\text{Se}_3$  are among the most popular materials of this class because of a single Dirac cone located inside the (narrow) bulk bandgap [2]. In addition, the unique thermoelectric properties of  $\text{Bi}_2\text{Te}_3$  have given rise to extensive studies of this material [3].

High-quality epitaxial layers are of particular importance for potential applications; among several available systems,  $\text{BaF}_2$  is an excellent substrate for the growth of bismuth chalcogenides [4]. The in-plane lattice constant of the highly symmetric layered structure consisting of  $X(1)\text{--Bi--}X(2)\text{--Bi--}X(1)$  quintuples ( $X = \text{Te, Se}$ ) matches well with that of the cleaved (111) surfaces of  $\text{BaF}_2$ . Because  $\text{BaF}_2$  is transparent for exciting and scattered light, the epitaxial layers are accessible in Raman measurements from both the surface and the film–substrate interface. We compare these data to assess

crystalline quality along the direction of growth. Finally, we have complemented the Raman studies with spectro-ellipsometric measurements aimed primarily at the determination of the penetration depth of light.

## 2. Experiment

Bismuth telluride and selenide layers were grown by molecular beam epitaxy in a Riber 1000 system under ultrahigh vacuum conditions as described in detail in [4]. The substrates were freshly cleaved (111)  $\text{BaF}_2$  single crystals kept at 300–400 °C during growth; with the deposition rate of 1–2 Å s<sup>-1</sup> the resulting film thicknesses spanned the range from 20 to 1000 nm. Samples for spectroscopic studies were selected from several series of deposition runs according to the results of high-resolution x-ray diffraction, displaying single-crystalline and single-phase ( $\text{Bi}_2\text{Te}_3$  or  $\text{Bi}_2\text{Se}_3$ ) materials oriented with their *c*-axis perpendicular to the (111) surface.



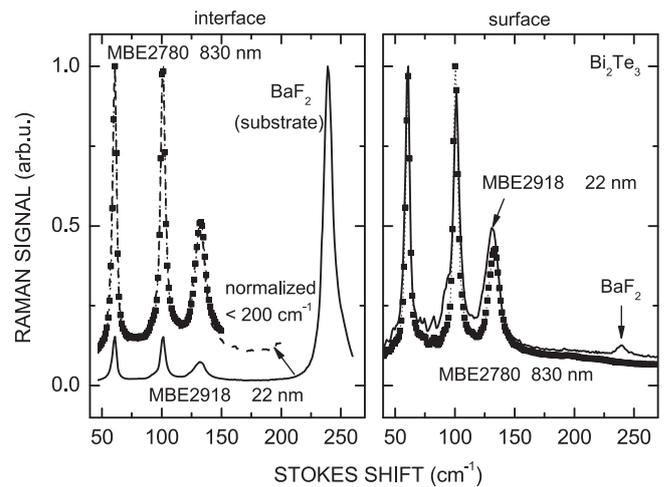
**Figure 1.** Schematic representation of the collection of Raman signals from the surface (left: the epilayer is in the focus of the lens) and the film–substrate interface (right: the substrate–epilayer interface is in the focus of the lens) of epitaxial films on BaF<sub>2</sub> substrate.

Unpolarized Raman spectra were acquired with a Renishaw InVia spectrometer at room temperature in back-scattering geometry. The exciting beam of a 50 mW, 632.8 nm HeNe laser was focused on either the front-side surface or the backside of the films through the transparent BaF<sub>2</sub> substrate; the two configurations are shown schematically in figure 1. With a 20x objective lens, the diameter of the spot size was about 10  $\mu$ m, and the laser power was kept low enough to avoid local heating. Our films were in good thermal contact with the massive ( $\sim 10 \times 10 \times 1$  mm<sup>3</sup>) substrate, and avoiding degradation by exciting light was fairly easy. We also registered several spectra with increased laser exposure in both intensity and duration in order to monitor possible damage to our samples.

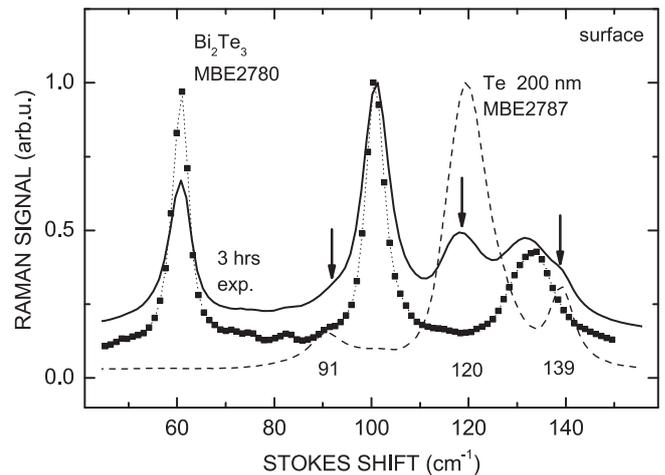
The optical response was determined by ellipsometric measurements using a Woollam VASE instrument at several angles of incidence. We chose films thick enough to be opaque in the 1.0–6.5 eV spectral range to prevent reflections at the film–substrate interface. The ellipsometric angles were converted to the complex permittivity and related response functions by way of approximating the sample by half-infinite material. Because the main purpose of these measurements was an estimate of the penetration depth of light, the use of pseudodielectric functions turned out to be justified. Due to the large refractive indices, the ellipsometric response was dominated by the in-plane polarizability of the optically uniaxial materials.

### 3. Results and discussion

The Raman spectra of two Bi<sub>2</sub>Te<sub>3</sub> epilayers shown in figure 2 display three strong bands, corresponding to the normal modes of A and E symmetry [5]. In spite of a very good signal-to-noise ratio, our data did not reveal the low-frequency E<sub>g</sub> vibration reported at 35.6 cm<sup>-1</sup> in the bulk Bi<sub>2</sub>Te<sub>3</sub> [6] nor its counterpart in the Bi<sub>2</sub>Se<sub>3</sub> expected at  $\sim 45$  cm<sup>-1</sup>; we suggest that the observation of these low-frequency modes is

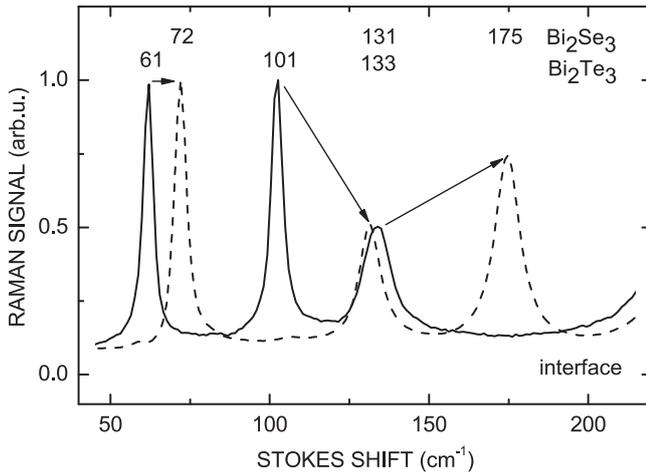


**Figure 2.** Normalized Raman spectra of 830 nm (symbols) and 22 nm (solid lines) Bi<sub>2</sub>Te<sub>3</sub> epilayers taken at the film surface (right panel) and the interface (left panel) with the BaF<sub>2</sub> substrate. Dashed line in the left panel: the spectrum of the thinner film normalized at lower wavenumbers (excluding the substrate band at 240 cm<sup>-1</sup>).

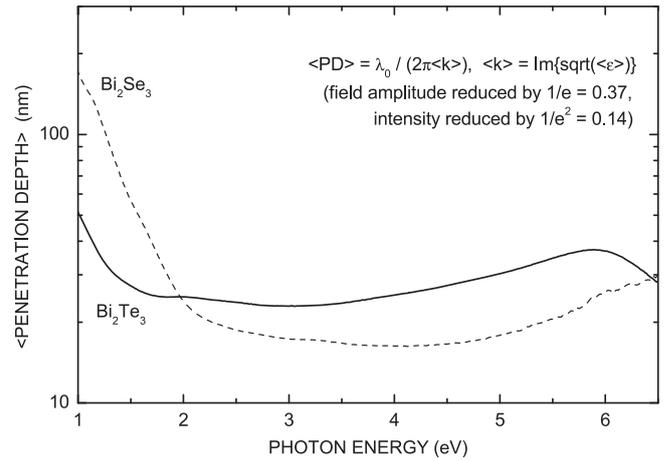


**Figure 3.** Normalized Raman spectra of the 830 nm-thick Bi<sub>2</sub>Te<sub>3</sub> layer measured on an as-grown spot with low excitation power (symbols) and after 3 h of exposure to increased excitation (solid line). Dashed line: the spectrum of the 200 nm-thick Te layer.

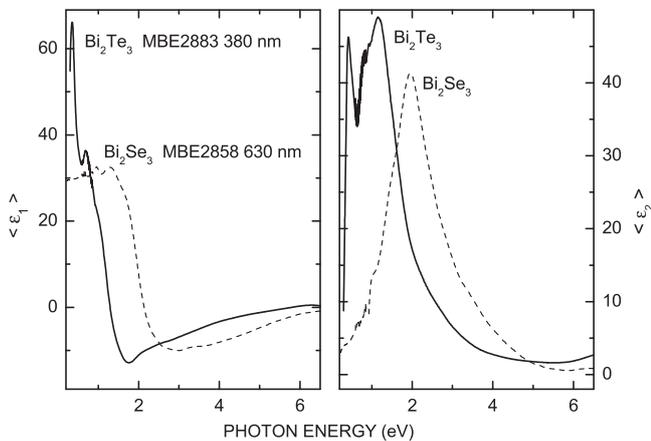
still an open question. The band at 240 cm<sup>-1</sup> results from the substrate; it is visible in the spectra of the 22 nm film (as measured from the surface). Contrary to the findings of [7], we did not observe the (unexpected) band at  $\sim 120$  cm<sup>-1</sup> in our thin films. On the other hand, several additional weaker bands appear in the spectra of the thin film when measured at the surface side (see the right panel of figure 2). The same sample yields spectra almost identical to those of thicker films when measured at the film–substrate interface (left panel of figure 2). We assign tentatively the additional bands to the vibrations of films with incomplete cells of Bi<sub>2</sub>Te<sub>3</sub> (the unit cell consists of three quintuples of 1.01 nm each; i.e., its thickness is 3.03 nm) and/or incomplete uppermost quintuples. We also did not observe the pair of bands at 93 and 113 cm<sup>-1</sup> reported in Raman scattering of thin ( $\sim 10$  nm) films



**Figure 4.** Raman spectra of  $\text{Bi}_2\text{Te}_3$  (solid line) and  $\text{Bi}_2\text{Se}_3$  (dashed line) epilayers taken at the film–substrate interface. The arrows connect bands of the same symmetry.



**Figure 6.** Penetration depth of light in  $\text{Bi}_2\text{Te}_3$  (solid line) and  $\text{Bi}_2\text{Se}_3$  (dashed line).



**Figure 5.** Real (left panel) and imaginary (right panel) parts of the pseudodielectric functions of  $\text{Bi}_2\text{Te}_3$  (solid lines) and  $\text{Bi}_2\text{Se}_3$  (dashed lines) epilayers.

grown on  $\text{SiO}_2$  [8]; the latter were interpreted as due to inversion symmetry breakdown in thin nanoplates of  $\text{Bi}_2\text{Te}_3$ .

We observed spurious Raman bands in measurements with increased excitation. Shown in figure 3 is a spectrum resulting after long exposure to the laser light, showing a broader triplet of the vibrations of  $\text{Bi}_2\text{Te}_3$  overlapping with one strong band at 120 and two weaker bands at  $\sim 140$  and  $\sim 90 \text{ cm}^{-1}$  (vertical arrows in figure 3). We interpret this finding as the result of the migration of Te toward the surface due to the elevated temperature and probably also the presence of Te vacancies. In fact, our measurement of a sample covered with a thick (200 nm) film of pure Te provided the spectrum, also shown in figure 3, with three bands at 91, 120, and  $139 \text{ cm}^{-1}$ ; they are in agreement with the room-temperature positions of  $92.2$ ,  $120.4$ , and  $140.7 \text{ cm}^{-1}$  found for bulk Te in Ref. [9].

The vibrational bands of  $\text{Bi}_2\text{Se}_3$  are shifted to higher frequencies with respect to those of  $\text{Bi}_2\text{Te}_3$  (see figure 4). The positions are in substantial agreement with the square root of

**Table 1.** Penetration depth of light (nm).

Photon energy (eV)	1.17	1.58	1.96	2.33	2.41	2.81	3.82
Wavelength (nm)	1060	785	633	532	514	442	325
$\text{Bi}_2\text{Te}_3$	37.7	26.2	24.9	24.1	23.9	23.0	24.6
$\text{Bi}_2\text{Se}_3$	125	49.7	25.5	19.6	19.1	17.7	16.3

the mass ratio, 1.27, and with the results obtained on bulk samples [5]. The main difference between the two materials consists in different Raman cross sections of the resolved phonons. The widths of all three bands are small, confirming the good structural quality of our epitaxial layers [4].

The results of ellipsometric measurements are shown in figure 5. They are in qualitative agreement with the early results of reflectance measurements followed by Kramers-Kronig analysis [10]. The spectral weight due to the interband electronic transitions is shifted by about 1 eV toward lower energies in  $\text{Bi}_2\text{Te}_3$ , and the onset of strong absorption is much steeper (see the strong and narrow band at  $\sim 0.4 \text{ eV}$ ). The low-energy parts of the spectra confirm significant differences between these two compounds in the configuration of the lowest conduction and highest valence states [11].

The fundamental optical spectra provide the penetration depth of light. We show in figure 6 this quantity calculated from the pseudodielectric function. In most of the visible range, its values are smaller than 30 and 20 nm for  $\text{Bi}_2\text{Te}_3$  and  $\text{Bi}_2\text{Se}_3$ , respectively. We have limited the spectral range here to avoid complications due to the interface and back-face reflections occurring in the transparent regime at low photon energies.

For convenience, we list the penetration depth in table 1 for selected photon energies of widely used lasers. The errors introduced by the neglected presence of surface overlayers and roughness are probably less than  $\sim 5\%$  of the listed values.

#### 4. Conclusion

We observed three narrow Raman bands in Bi<sub>2</sub>Te<sub>3</sub> and Bi<sub>2</sub>Se<sub>3</sub> out of the four resulting from crystalline symmetry, confirming the excellent quality of the epitaxial films. Additional bands were observed after excessive exposure to exciting light, consistent with the migration of Te to the sample surface. In-plane optical spectra, including those of the penetration depth of light, were obtained from ellipsometric measurements.

#### Acknowledgments

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