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Preliminary studies of the Raman spectra of Ag_2Te and Ag_5Te_3

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Abstract The theoretical calculations indicated that the monoclinic low-temperature phase of silver telluride (β-Ag_2Te) is a new binary topological insulator with highly anisotropic single Dirac cone surface. We obtained β-Ag_2Te crystal ingots containing few grains by the Bridgman method. We also deposited thin films of tellurium, Ag_5Te_3 and (Te+Ag_5Te_3) by thermal evaporation method. The Raman spectra of β-Ag_2Te, tellurium and Ag_5Te_3 were measured at three excitation wave lengths: 633, 515 and 488 nm. The Raman active modes of β-Ag_2Te, tellurium and Ag_5Te_3 are situated at frequencies below 300 cm^{-1} while vibrations of other phases appear at higher frequencies.

Keywords Semiconductors · Single crystals · Thin films · Raman spectroscopy

1 Introduction

Silver telluride (Ag_2Te), one of the silver chalcogenides, is known as the Hessite mineral in nature. It has some unique properties such as superionic conductivity and [as it was recently

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shown by Zhang et al. (2011)] theoretical calculations indicated that the low-temperature phase (β-Ag_2Te) is a binary topological insulator with highly anisotropic single Dirac-cone surface. The band-gap values of β-Ag_2Te reported in literature are inconsistent and vary from 0,01 up to 1.7 eV (Dalven 1966; Prabhune and Fulari 2009). Moreover, the Raman spectrum is also not yet clarified—the interested researcher could easily find information as to what feature in the Raman spectrum of Ag_2Te samples does not belong to the Ag_2Te vibrations—Qin et al. (2007).

We recently presented a thorough study of the broadband reflectance spectrum of Ag_2Te and determined the plasma energy of Ag_2Te to be 0.097 eV and the bandgap $E_g = 1.44$ eV—Hong et al (2013). Lee et al. (2012) established extremely high electron mobility in Ag_2Te nanowires (over 22,000 cm^2/Vs—see Lee et al. 2012). This makes monoclinic Ag_2Te a possible choice for material for FET detectors of THz radiation.

Here we present results on the synthesis of Ag_2Te crystals and deposition of thin films of pure Te and Ag_5Te_3 as well as films with mixed phases by thermal evaporation and their study by Raman spectroscopy.

2 Experimental

Ag_2Te monoclinic crystals typically containing few grains were grown by the Bridgman method. In order to clarify the Raman spectrum of monoclinic Ag_2Te besides the main object of our study (β-Ag_2Te) we have to examine specimens with different compositions: pure tellurium, Ag_5Te_3 (as some residual quantities of Ag_5Te_3 could be found in Ag_2Te ingots) and two-phase films consisting of tellurium and Ag_5Te_3 (by analogy). This problem was simply solved by deposition of thin films by thermal evaporation technique and by varying the deposition rate and time thin films of different compositions were obtained. The thickness of deposited films is controlled during the process by a build-in detector. The exact values of the deposition rate and films' thickness are summarized in Table 1.

The qualitative analysis of the Ag_2Te crystals and the thin films was performed by X-ray powder diffraction in Philips PW1050 diffractometer, equipped with a Cu K_α tube. In order to determine the exact orientation of surface of the specimen for Raman spectroscopy we examined each of the examined surfaces by XRD on the same diffractometer. The data were collected in θ–2θ step-scan mode in the angle interval from 20° to 50° (2θ) at steps of 0.05° (2θ) and counting time of 3 s/step. The phase homogeneity and composition of the deposited films was determined by a SEM/EDX study in a LYRA/TESCAN scanning electron microscope equipped with Brucker Quantax 400 unit for EDX measurements.

Table 1 Results of phase homogeneity and composition studies of polycrystalline Ag_2Te and thin film specimens

Specimen	Ag_2Te ingot	Thin films		
Film thickness/rate of deposition		10 nm/0.5 Å/s	350 nm/1.2 Å/s	600 nm/ 0.9 Å/s
Phases	Single phase	Single phase	Single phase	Two phases
Composition	100 % Ag_2Te	Pure Te	Ag_5Te_3	Dark phase denoted as PEAK in Fig. 2: (65 % Ag_5Te_3 +35 % Te) Bright phase denoted as FLAT in Fig. 2: Ag_5Te_3

Raman spectra were measured using HORIBA Jobin Yvon Labram and an Ar^+ laser (for 515 and 488 nm excitation wavelengths) and a He–Ne laser for 633 nm excitation. The irradiated spot and the absolute accuracy were 5 μm and 0.5 cm^{-1}, respectively. The laser power was limited to 300 μW in order to prevent damages of the studied specimens in most of measurements. Some Raman spectra were excited at higher laser power to investigate irradiation-induced changes in the samples.

3 Results and discussion

3.1 XRD and SEM

The XRD powder pattern (Fig. 1 upper trace) coincides with the data published by Schneider and Schulz (1993) for monoclinic Ag_2Te. The XRD pattern of the plane perpendicular to the growth axis of a Ag_2Te crystal grown by the Bridgman method implies the conclusion that the irradiated area is single crystalline and is parallel to the $(\bar{2}12)$ plane—see Fig. 1 lower trace.

The phase homogeneity and composition are studied by powder XRD analysis and SEM/EDX observations and measurements. It is established that only specimens of about 600 nm thick layers consist of two phases—see Fig. 2. The brighter phase, denoted as FLAT in Fig. 2 has composition of pure Ag_5Te_3 while the darker one, denoted as "PEAK" in Fig. 2 has composition of (65 % Ag_5Te_3 + 35 % Te). The results of XRD and SEM/EDX study are summarized in Table 1.

3.2 Raman spectrum of Ag_2Te

Our experience shows that Ag_2Te is very soft material and we have not yet found a suitable etching agent for its chemical polishing. For this reason we used for Raman spectroscopic measurements the as grown $(\bar{2}12)$plane, which is the plane perpendicular to

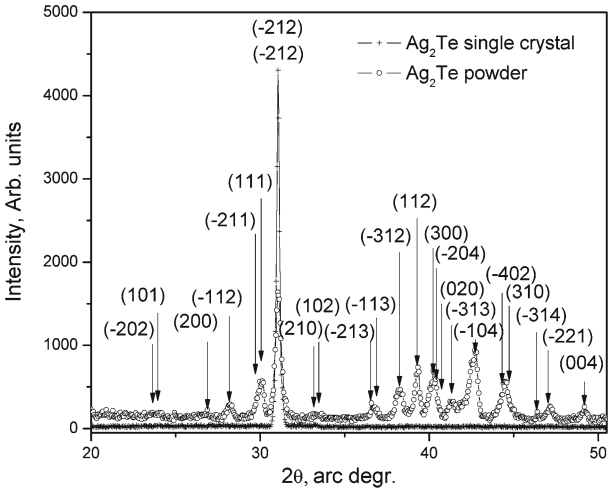

Fig. 1 Powder X-ray diffraction (XRD) pattern of Ag_2Te- upper trace and XRD of the $(\bar{2}12)$plane (perpendicular to the growth axis)—lower trace

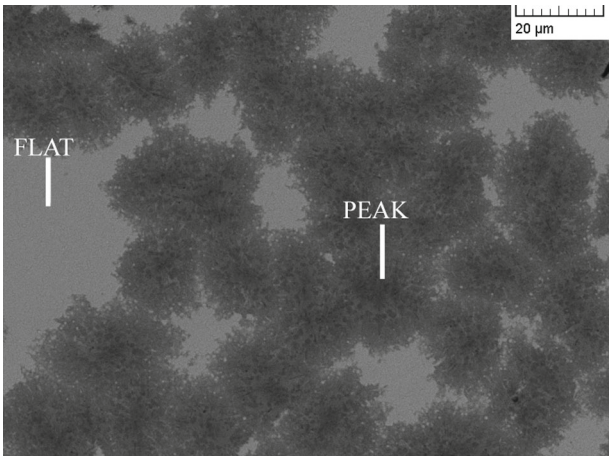

Fig. 2 The back-scattered electron SEM image of 600 nm thick layer. The bright phase marked by "FLAT" in the image consists of pure Ag_5Te_3. The darker one, denoted as "PEAK" has composition of (65 % Ag_5Te_3 + 35 % Te)

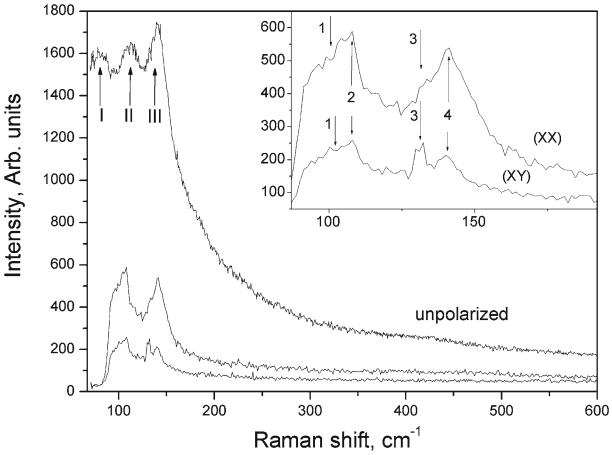

Fig. 3 Unpolarized and (XX) and (XY) polarized Raman spectra of Ag_2Te. The magnified low-frequency part of the polarized spectra is shown in the inset

the growth axis. Prior to the measurements the specimen was ultrasonically cleaned initially in ethanol and further in acetone. The polarized Raman measurements were carried out in back-scattering geometry in parallel (XX) and perpendicular (crossed; XY) configuration.

The full vibrational representation of Ag_2Te at $\mathbf{k} = 0$ contains $\Gamma = 3A_g + 3B_g + 3A_u + 3B_u$ modes (space group P $2_1/c$ (No. 14), unique axis **b** and point group $C_{2h}(2/m)$). The A_g and B_g modes are Raman active, while A_u and B_u modes are IR active (see Aroyo et al. 2006a,b).

The Raman spectrum of polycrystalline Ag_2Te sample is shown in the Fig. 3—upper trace. Three broad bands with full width at a half maximum (FWHM) of about 18–20 cm^{-1} and centered at about 80, 110 and 138 cm^{-1} are distinguishable. The high values of the FWHM tends to suspicion that these features consists of more than one mode. We conduct

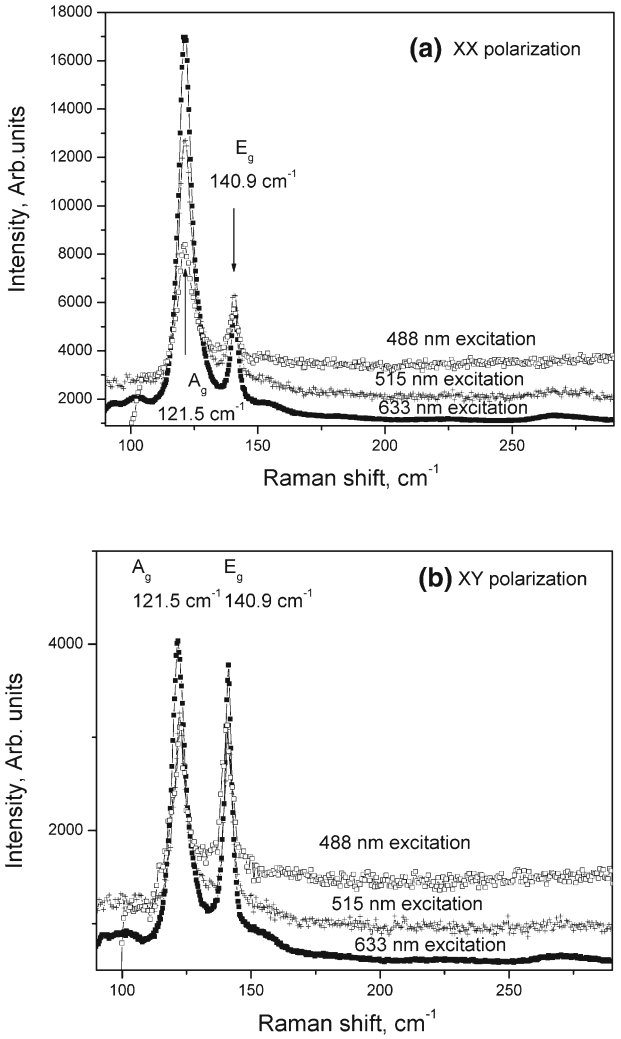

Fig. 4 **a** XX-polarized Raman spectra of 10 nm thick pure tellurium layer excited at 633, 515 and 488 nm laser wavelengths; **b** same as (**a**) in XY polarization—see text

additional measurements of the polarized Raman spectra of β-Ag_2Te single crystal. The notch filter cuts the wavelengths below 90 cm^{-1} and therefore the band centered at about 80 cm^{-1} is impossible to be studied further. Then we suggest that the band situated at about 138 cm^{-1} includes two modes: marked by 3 at 131 and marked by 4 at 140 cm^{-1}. Another band seems also complex and two modes (marked by 1 at 101 cm^{-1} and marked by 2 at 108 cm^{-1}) are supposed to form the feature centered at about 110 cm^{-1}. Moreover, the intensity ratio I_2/I_4 of the modes 2 and 4 remains unchanged while the intensity ratio I_4/I_3 significantly drops upon change of the scattering geometry from (XX) to (XY) scattering geometry. We therefore tentatively ascribe line 3 to a B_{g-} and line 4 to an A_{g-} vibration. We do not observe any other feature in the higher frequency part of the Raman spectrum of Ag_2Te crystals.

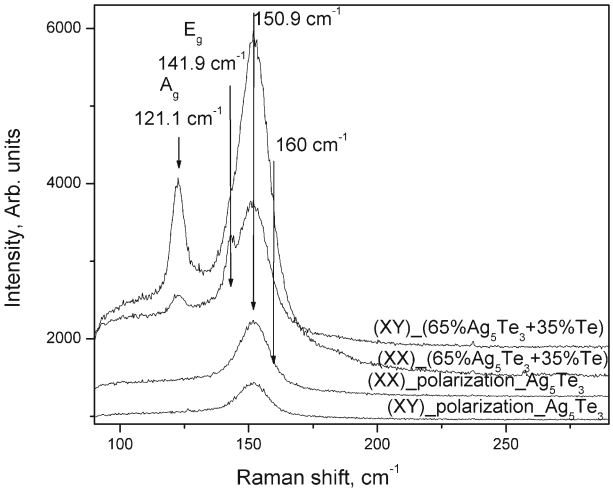

Fig. 5 (XX) and (XY) polarized Raman spectra of about 600 nm thick layer containing (Ag_5Te_3) and (65 % Ag_5Te_3 + 35 % Te) phases

3.3 Raman spectrum of pure tellurium and Ag_5Te_3

According to the binary phase diagram Ag–Te (see for example Karakaya and Thompson (1991)) there are only three phases stable at room temperature: Ag_2Te, Ag_5Te_3 and Te. In this sense, the Raman spectrum of Te and Ag_5Te_3 should also be measured in order to accurately establish the spectrum of Ag_2Te. We observed two clearly distinguishable modes in the Raman spectrum of pure tellurium—Fig. 4a and b: the A_g mode at 121 cm^{-1} and E_g mode at 141.9 cm^{-1}. These modes practically coincide with those described by Pine and Dresselhause (1971)—120.4 and 140.7 cm^{-1}, respectively. The frequency of these vibrations does not depend on the wavelength of the exciting laser light.

The Raman spectrum of Ag_5Te_3 in the frequency range 90–1,200 cm^{-1} (see Fig. 5) contains a broad feature at about 150 cm^{-1} and a weak feature at about 159 cm^{-1}, distinguishable in parallel scattering geometry.

3.4 Raman spectra of Ag_2Te specimens damaged by the laser beam

We also performed Raman measurements on Ag_2Te single crystal specimens irradiated with laser power higher than 0.5 mW in order to evaluate the Raman spectrum of phases decomposing due to laser-induced heating. We present in Fig. 6 the Raman spectra of specimens irradiated with laser power of 0.7 mW at 633 nm (upper trace) and with 20 and 40 mW at 515 nm (middle trace and lower trace, respectively). We focused the laser beam on a spot of diameter of 5 μm in all measurements in order to retard the decomposition process.

It is clearly distinguishable that too strong laser-beam irradiation causes an Ag_2Te phase decomposition according to the following the redox reaction (Qin et al. 2007):

$$Ag_2Te + O_2 \rightarrow 2Ag + TeO_2, \quad (1)$$

The Raman spectra of the specimens exposed to higher laser power consist of the spectra of different polymorphic forms of tellurium oxide (Te_2O). The spectrum measured at lower laser power (0.6 mW at 633 nm wavelength) (see the BR1-marked upper trace in Fig. 6) is

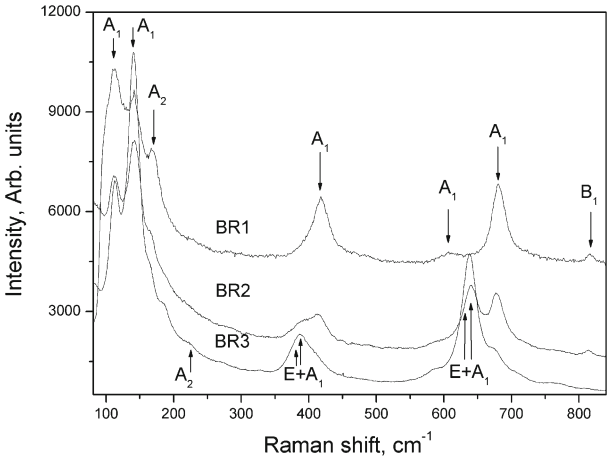

Fig. 6 Unpolarized Raman spectra of Ag_2Te single crystal specimens excited at 633 nm with 0.6 mW laser power (BR1-marked upper trace), at 515 nm with 20 mW laser power-BR2 marked middle trace and at 515 mW with 40 mW laser power-BR3 marked lower trace

dominated by vibrations of the metastable γ -TeO_2– see Champarnaud-Mesjard et al. (2000): A_1 and B_1 modes at 115, 140, 173, 417, 608 and 680, and 816 cm^{-1}, respectively. The stable α- and β- polymorphic forms of TeO_2 (Kondratyuk et al. 1987 and Beyer 1967) are achieved by increasing the laser power to 20 and 40 mW at 515 nm wavelength, respectively.

The spectrum excited with the highest laser power (BR3-marked lower trace in Fig. 6) could be attributed to a mix of α- and γ -TeO_2 dominated by α -TeO_2 (Champarnaud-Mesjard et al. 2000 and Mirgorodsky et al. 2000) and contains A_1, A_2 and E-modes of α - TeO_2 at: 390, 643 and 379, 642 and 225 cm^{-1}, respectively. The shoulders at about 180 cm^{-1} and at about 672 cm^{-1} (not marked in Fig. 6) could be ascribed to coinciding B_{1g} and B_{3g} and A_g modes of β-polymorphic forms of TeO_2– Mirgorodsky et al. (2000).

The spectrum excited with 20 mW (515 nm excitation wavelength) contains simultaneously modes of α-, β- and γ -TeO_2– see Fig. 6—middle trace.

4 Conclusions

We successfully synthesized crystals of the monoclinic (β-phase) of Ag2Te and deposited thin films of Te and Ag_5Te_3 and of mixed phases [Ag_5Te_3+ (65 % Ag_5Te_3+ 35 % Te)]. The obtained Raman response from the crystals and thin films enables us to conclude that the Raman spectrum (in the spectral range 70–600 cm^{-1}) of β -Ag_2Te consists of two bands at 111 and 134 cm^{-1} and a broad feature at about 80 cm^{-1}. We suggest that the bands arise due to merging of B_g and A_g modes at 101 and 108 cm^{-1} and most probably 2 A_g modes at 131 and 141 cm^{-1}, respectively. The Raman spectrum of Ag_5Te_3 in the same frequency range contains a broad feature at about 151 cm^{-1} and a weak shoulder at 159 cm^{-1}, while that of pure tellurium exhibits an A_g mode at 121 cm^{-1} and an E_g mode at 141 cm^{-1}. We establish that excitation by a laser power higher than 350 μW decomposes Ag_2Te to silver and different polymorphic forms of tellurium oxide TeO_2.

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