# Investigation of Bi-Te Films with Controlled Nanostructure

A. Bailini[1], F. Donati[1], M. Zamboni[1], V. Russo[1], M. Passoni[1], C.S. Casari[1], A. Li Bassi[1]*, C.E. Bottani[1]

[1] NEMAS - Center for NanoEngineered MAterials and Surfaces and Dipartimento di Ingegneria Nucleare, Politecnico di Milano, Via Ponzio 34/3, 20133 Milano, Italy

*corresponding author: andrea.libassi@polimi.it, tel. +39 0223996316, fax +39 0223996309

**Abstract**

The possibility to produce films with a controlled nanostructure has recently driven the interest towards new materials where the thermoelectric figure of merit $Z$ can in principle be improved by decreasing the phonon thermal conductivity due to scattering at grain boundaries. Bismuth telluride ($Bi_2Te_3$) is the most common thermoelectric material for cooling applications at room temperature, nevertheless a detailed comprehension of the effects of nanostructuring on the thermoelectric properties is still lacking. Moreoever, thermoelectric properties of less known compounds of the Bi-Te system, such as BiTe and $Bi_4Te_3$, have not been investigated yet.

In this work ns UV Pulsed Laser Deposition (PLD) has been used to produce a large variety of micro and nanocrystalline Bi-Te films with different morphology, stoichiometry and structure. By tuning deposition parameters (ambient gas pressure, substrate temperature, laser fluence) crystalline films were obtained with composition ranging from 20% at. Bi to 65% at. Bi. The film morphology and stoichiometry were investigated by SEM and EDS, while structure and phases by Raman spectroscopy and XRD. Seebeck coefficient and electrical resistivity were measured for $Bi_2Te_3$, BiTe and $Bi_4Te_3$.

**Introduction**

Bismuth telluride is a V-VI compound semiconductor with a small gap [1], widely studied for its thermoelectric properties [2]. The $Bi_2Te_3$ crystal structure has a hexagonal conventional unit cell with a -($Te^1$-Bi-$Te^2$-Bi-$Te^1$)- layer structure stacked along the $c_H$ axis [3,4], with $Te^1$-$Te^1$ bond of van der Waals type. The Bi-Te phase diagram [5] indicates that $Bi_2Te_3$ is a stable phase at room temperature in a narrow range of composition centered at about 40% at. Bi. Mineral phases with compositions other than $Bi_2Te_3$ have been found and studied [6-8]. Recent studies suggest that phases different from $Bi_2Te_3$ could in principle be interesting as thermoelectric materials [8,9].

The $Bi_2Te_3$ thermoelectric figure of merit ZT at room temperature is nearly unit [2]; this represents a limit in a number of applications. Theoretical studies have predicted an increment of ZT up to 10-15 for low-dimensional materials [10]. Different deposition techniques have been employed to produce low dimensional structures of Bi [11], $Bi_2Te_3$ [12-17], skutterudites [18], PbTe [19], metal oxides [20] and Si/SiGe [21].

In particular, for polycristalline thin films, the improvement of Z should be due to a decrease of the phononic thermal conductivity caused by phonon scattering at grain boundaries. High performance $Bi_2Te_3$ thin films can be employed in Peltier-cooling microdevices [22], and it would be extremely interesting to be able to control the film nanostructure, both to improve the film thermoelectric performances and to achieve a better comprehension of the relationship between transport properties and film structure in non-ideal systems. Pulsed Laser Deposition (PLD) is a very attractive technique to this purpose since it combines a high deposition rate with a great versatility in the deposition of films with a multi-element stoichiometry and with a variety of structures, from amorphous to polycrystalline or even epitaxial [23]. Only a few attempts of $Bi_2Te_3$ film deposition by PLD are reported in the literature [13-17], witnessing the difficulty of producing films with the correct composition and controlled morphology and crystallinity.

We here present a detailed investigation of Bi-Te films deposited by PLD and we report on the experimental conditions leading to the growth of polycrystalline $Bi_2Te_3$ thin films, showing how the film crystallinity (orientation, grain size) and morphology can be controlled by playing with deposition temperature, background pressure and choice of the substrate. Also, Bi-Te thin films with a great variety of compositions can be obtained, and we report about the influence of the composition on the structure of the films, exploring the formation of Bi-rich or Te-rich phases. For the first time we show a Raman characterization of the BiTe and $Bi_4Te_3$ phases, supported by XRD and EDS measurements and correlated to group theory predictions. First measurements of Seebeck coefficient and electrical resistivity were measured for $Bi_2Te_3$, BiTe and $Bi_4Te_3$ compounds with compact morpholgies.

**Experimental details**

Bismuth telluride films have been grown by PLD on Si and mica substrates at different temperatures in the range 30-480 °C. UV pulses (duration 10-15 ns) from a KrF excimer laser ($\lambda$ = 248 nm, 10 Hz) were focused on a Bi-Te target with a fluence F on the target ranging from 0.9 to 9 J/cm$^2$. Targets were made of sintered powders of Bi and Te with different compositions (20%, 30% and 40% at. Bi). Films were grown in vacuum and inert gas (Ar) pressure P (1 – 200 Pa); target-to-substrate distance $d_{T-S}$ was 50 mm. The number of laser pulses (10.000 – 30.000) was chosen in order to obtain film thickness about 0.5-1 μm as measured by a quartz microbalance depending on experimental parameters. Film morphology and composition (measurement precision ±1%) were analyzed with a FE-SEM Zeiss Supra 40 equipped with Oxford EDS. Raman spectra were acquired with a triple grating Jobin Yvon T 64000 spectrometer (excitation at 532 nm from a Nd:YAG laser in backscattering configuration), while XRD diffractograms were obtained with a PANalytical X'pertPro (Cu K$\alpha$, $\lambda$=1.54 Å) in θ-2θ configuration. Thermolectric properties were measured in a HV chamber (pressure $< 10^{-4}$ Pa).

## Results and discussion

We have explored the ranges of the PLD experimental parameters leading to deposition of films composed by $Bi_2Te_3$ only, and we have found that these correspond to films with a Bi atomic content in the range 40%-42.5%. In particular, we found a set of values for the background inert gas pressure (10-200 Pa Ar), for the laser fluence ($\leq$ 1.2 J/cm$^2$) and for the deposition temperature (250°-350°C) in order to obtain films with the $Bi_2Te_3$ composition starting from a target with 40% at. Bi content.

At P(Ar) < 10 Pa the deposited films are considerably rich in Bi (it is known that ablation in vacuum leads to a Bi-rich film [15,16]); in fact Te species are lighter than Bi species, and the Te plume expands over a wide angle at low background pressures, while at higher pressures it is strongly confined in the forward direction, like the Bi plume, thus allowing reproduction of the target composition in films deposited along the plume axis.

If we now consider films deposited at P(Ar) $\geq$ 10 Pa, we observe that when the fluence increases from 0.9 to 9 J/cm$^2$ (while keeping deposition temperature $\leq$ 350°C, see below), the Te content in the film decreases very rapidly, as already reported [14-16]. This has been ascribed to sputtering from the film of the more volatile and lighter Te atoms by highly energetic species [13]. Fluence values below 1.2 J/cm$^2$ must thus be employed to obtain $Bi_2Te_3$ film. As for the substrate temperature, for T > 350°C (while F $\leq$ 1.2 J/cm$^2$) films begin to enrich in Bi [15,16], probably due to re-evaporation of deposited Te from the substrate [14].
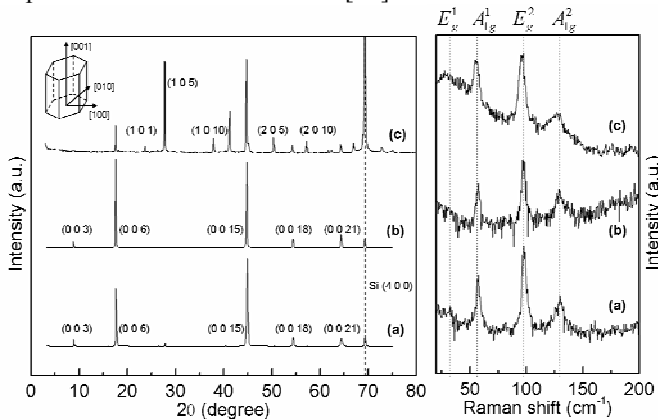


**Fig.1**: XRD (left) and Raman spectra (right) of $Bi_2Te_3$ films deposited at substrate temperature of 350°C, at laser fluence of 0.9 J/cm$^2$ and at (a) 10 Pa Ar, (b) 40 Pa Ar and (c) 200 Pa Ar.

In fig.1 we present Raman and XRD spectra corresponding to films deposited using deposition parameter values in the ranges that lead to the 40% at. Bi-60% at. Te composition. The Raman spectrum of $Bi_2Te_3$ is characterized by 4 modes [24,25]: $E_g^1$ at 36.5 cm$^{-1}$, $A_{1g}^1$ at 62 cm$^{-1}$, $E_g^2$ at 102.3 cm$^{-1}$ and $A_{1g}^2$ at 134.0 cm$^{-1}$. Raman and XRD spectra present only the characteristic $Bi_2Te_3$ peaks and reflections. We found that films produced by PLD are composed only of the $Bi_2Te_3$ phase when a film composition between 40% at. Bi and 42.5% at. Bi is obtained.

PLD deposition parameters can also be used to control the film crystallinity (orientation, grain size) and

morphology (fig.2). For the films (a) and (b) in fig.2, deposited at 10 and 40 Pa Ar respectively, only XRD peaks corresponding to the [0 0 n] growth direction of the hexagonal cell are detected (fig.1), confirming a preferential growth direction with the $c_H$ axis perpendicular to the substrate. SEM images show layered structures mainly stacked in the vertical direction. On the contrary the morphology of the film (c), deposited at a high pressure value (200 Pa Ar), presents randomly oriented μm size hexagonal platelets (fig.2c). In this case the XRD spectrum (fig.1) also shows well defined (m 0 n) peaks, confirming a less directional growth. By measuring the width of (0 0 6) and (0 0 15) XRD reflections and applying Scherrer formula an average domain size of the order of 150-200 nm can be estimated for all the $Bi_2Te_3$ films.
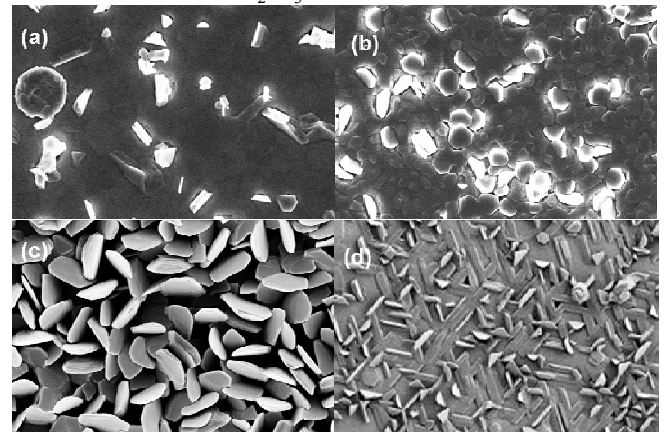


**Fig.2**: SEM images of $Bi_2Te_3$ films deposited at substrate temperature of 350°C, at laser fluence of 0.9 J/cm$^2$ and at (a) 10 Pa Ar on Si, (b) 40 Pa Ar on Si, (c) 200 Pa Ar on Si; and at (d) 10 Pa Ar on mica.

The temperature dependence of morphology has also been investigated: films deposited on Si at room temperature and at 150°C are composed of small irregular aggregates; increasing substrate temperature to 350°C leads to very compact films with few μm size crystals. The type of substrate affects only film morphology and not the film stoichiometry or crystalline structure. In particular we have observed that deposition on mica leads to a preferential growth of $Bi_2Te_3$ crystals along the lattice directions of the substrate (fig.2d). This oriented growth mechanism could be explained with van der Waals epitaxy [26], given the similar lattice parameters of $Bi_2Te_3$ and mica, and could in principle influence transport properties introducing anisotropic effects.

XRD and Raman spectra of films with different compositions are reported in fig.3, fig.4 and fig.5, both for Bi-rich and Te-rich films. In this case deposition parameters are out of the defined ranges stated above. Bi-rich films are obtained starting from a 40% at. Bi target for high values of substrate temperature (350°-480°C) and laser fluence (1.2-9 J/cm$^2$), and for low gas pressure (vacuum-10 Pa Ar), while Te-rich films are obtained starting from a 20% at. Bi target for low values of substrate temperature ($\leq$250°C) and fluence ($\leq$1 J/cm$^2$), and for Ar pressure between 10 and 100 Pa.

Moving from the $Bi_2Te_3$ composition to films with Bi content higher than 40%, Raman spectra modify (fig.5). A progressive reduction of the intensity of $Bi_2Te_3$ peaks is observed together with the appearance of new broad, unknown features. In particular for films with 50% at. Bi content (which corresponds to the stoichiometry of the BiTe structure) two bands at 88 $cm^{-1}$ and 117 $cm^{-1}$ appear, while a broad band at 83 $cm^{-1}$ appears in the spectrum of the film with 57% at. Bi content (which corresponds to the stoichiometry of the $Bi_4Te_3$ structure). We interpret the new observed Raman features to vibrational modes of the BiTe and $Bi_4Te_3$ phases by comparing XRD spectra to those reported for these compounds [8,15]. For films with 50% at. Bi content, the (0 0 6) and (0 0 15) $Bi_2Te_3$ reflections are substituted by the (0 0 5) and (0 0 12) BiTe reflections, while for 57% Bi content the (0 0 9) and (0 0 21) $Bi_4Te_3$ peaks appear. At intermediate compositions (45% and 53% at. Bi), peaks of two phases are detected. From (a), (c) and (e) data of fig.3 we calculate lattice parameters for $Bi_2Te_3$ ($c_H$=3.0427 nm and $a_H$=0. 43919 nm), for BiTe ($c_H$=2.3993 nm and $a_H$=0.4432 nm) and for $Bi_4Te_3$ ($c_H$=4.1806 nm and $a_H$=0.4467 nm). Comparing these values with literature values [4,7] we notice a contraction of the $c_H$ parameter, maybe related to a stress state or to a small Te excess [8].
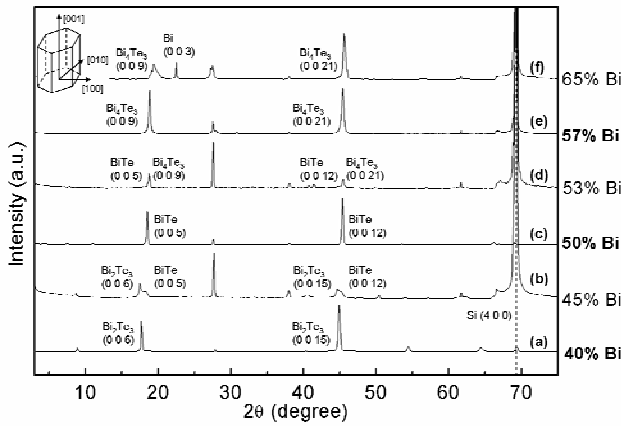
**Fig.3**: XRD spectra of Bi-Te films with Bi-content ranging from 40% to 100%.
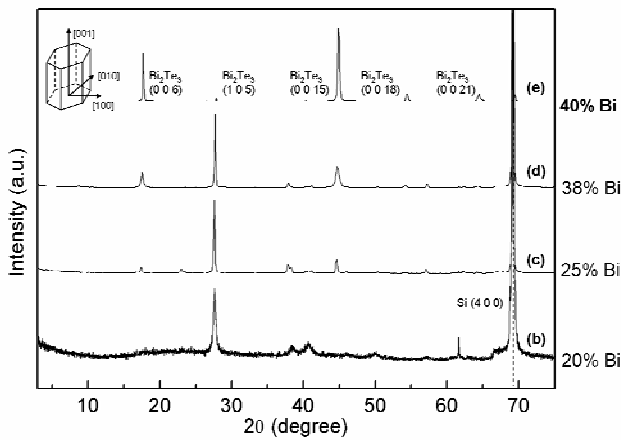
**Fig. 4**: XRD spectra of Bi-Te films with Bi-content ranging from 0% to 40%.

We observe that, with respect to group theory predictions [27], not all the expected Raman-active modes have been detected in the spectra: 12 Raman peaks are expected for BiTe ($6A_{1g} + 6E_g$) and 6 for $Bi_4Te_3$ ($3A_{1g} + 3E_g$), but the three compounds ($Bi_2Te_3$, BiTe, $Bi_4Te_3$) have the same crystal structure and very similar bonds and lattice parameters [7], so that peaks corresponding to some of the vibrational modes of different phases could have frequency shifts too close to each other, leading to the presence of broad bands.
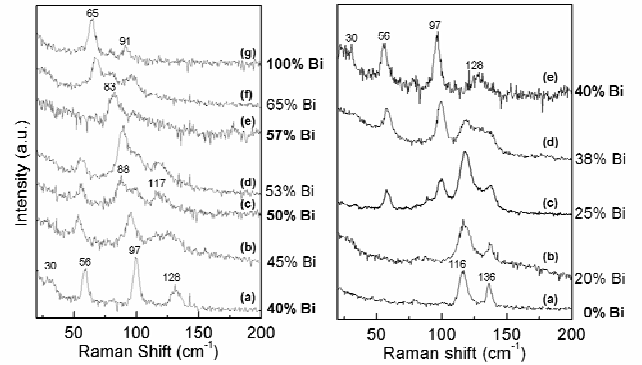
**Fig.5**: Raman spectra of Bi-Te films with Bi-content ranging from 0% to 100%.

Some examples of naturally occurring or synthesized Bi-Te phases even more rich in Bi than $Bi_4Te_3$ are reported in the literature [9]. We were able to obtain films with a high Bi atomic content (65% Bi, which is close to the stoichiometry of the $Bi_7Te_3$ structure), using critical deposition conditions as very high substrate temperature and fluence (480°C and 3.5 $J/cm^2$). However Raman and XRD spectra (fig.3 and fig.5) indicate coexistence of the above discussed phases with pure Bi, again with a (0 0 n) preferential growth direction.
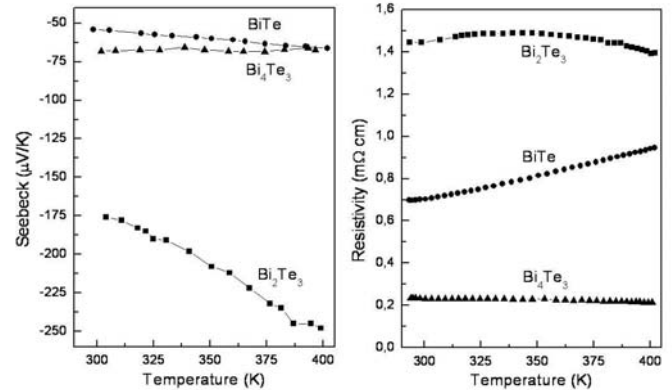
**Fig. 6**: Seebeck coefficient and electrical resistivity of $Bi_2Te_3$, BiTe and $Bi_4Te_3$ films.

The deposition of films with Te-rich composition, with respect to stoichiometric $Bi_2Te_3$, is more difficult, since lighter Te atoms can be sputtered after deposition by incoming energetic particles and they easily re-evaporate from the growing film at high substrate temperatures [5-8,10]. Films in this range of composition (i.e. < 40% Bi) were obtained starting from Te-rich targets. Raman spectra

of these films show the strong Te peaks at 116 cm$^{-1}$ (A$_{1g}$) and 136 cm$^{-1}$ (E$_g$) [28], even for Bi content close to the Bi$_2$Te$_3$ composition (up to 38.5% at. Bi), together with Bi$_2$Te$_3$ peaks. Te peaks rapidly become the unique features present in the spectrum for lower Bi contents (i.e. < 20%). This is to be ascribed to a greater Raman cross section for Te. No other phase seems to be produced in this range of composition, as confirmed by XRD spectra.

Preliminary measurements of Seebeck coefficient (α) and electrical conductivity (ρ) were performed in vacuum for Bi$_2$Te$_3$, BiTe and Bi$_4$Te$_3$ films (fig.6). All these systems show a n-type behaviour; Bi$_2$Te$_3$ films show α values decreasing with increasing temperature (up to -260 μV/K at 400 K, comparable to bulk material [2]); increasing Bi contents α is quite constant, with values ranging from -70 to -50 μV/K. Film resistivity approaches the Bi value increasing Bi contents: ρ decreases from ρ≈1.4 mΩ cm for Bi$_2$Te$_3$ (comparable to bulk material [2]), to ρ≈0.8 mΩ cm for BiTe to ρ≈0.2 mΩ cm for Bi$_4$Te$_3$.

## Conclusions

We have produced by PLD a great variety of Bi-Te films with different compositions. The detailed characterization of the films by Raman, XRD, SEM and EDS allowed us to investigate the structural properties not only of pure Bi$_2$Te$_3$ films, but also of films containing other less-known compounds as BiTe and Bi$_4$Te$_3$. In particular, for the first time we were able to attribute some Raman features to these Bi-rich phases, even though not all the expected Raman-active modes, as predicted by group theory, were observed.

Moreover, by varying the deposition temperature and the buffer gas pressure, different morphologies can be obtained, from a compact and oriented growth to an assembly of randomly oriented micrometer size crystals (at higher pressures). The crystal domain size is also influenced by deposition temperature and we guess that a better control on the grain size can be obtained with a post-deposition annealing treatment. This can be of interest to tune the film thermoelectric properties, since grain boundaries represent a barrier to phonon transport. Also the substrate type strongly influences growth mechanisms; on mica, at low pressure, the film grows along the substrate lattice directions because of van der Waals epitaxy.

Crystal structures more rich in Bi than Bi$_4$Te$_3$ were not obtained even in PLD films with a Bi content > 60%. Instead we observed a mixture of the above mentioned compounds with pure crystalline Bi (again characterized by the same hexagonal structure). No Te-rich phases were observed in films with a composition rich in Te (> 60% at. Te).

Preliminary measurements of Seebeck coefficient (α) and electrical conductivity (ρ) were performed in vacuum for Bi$_2$Te$_3$, BiTe and Bi$_4$Te$_3$ films. Bi$_2$Te$_3$ films show high α values comparable to bulk material [2]; BiTe and Bi$_4$Te$_3$ are less n-type. Film resistivity decreases increasing Bi contents, approaching the Bi value.

We believe that the wide range of structures that can be obtained by PLD is of interest in view of a fine control of the structural and morphological properties of thermoelectric films. This is necessary both for a detailed investigation of the relationship between structural and transport properties of polycrystalline materials and a check of theoretical predictions, and can open the way to the engineering of tailored Bi$_2$Te$_3$ thin films with improved thermoelectric properties.

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