Oriented crystallization of thin films that are obtained with the aid of a laser

Yu. A. Bykovskiĭ, A. G. Dudoladov, V. P. Kozlenkov, and P. A. Leont'ev

Moscow Engineering-Physics Institute
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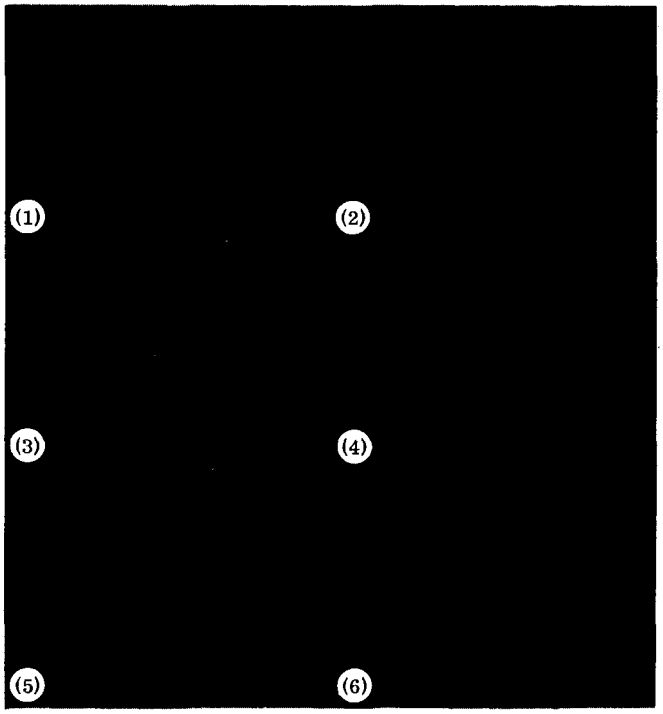
We present data on the deposition of thin films of bismuth telluride with the aid of a Q-switched laser. The energy flux density on the target surface was $\sim 10^9$ W/cm^2. The temperature of the NaCl and mica substrates was varied between 20 and 350 °C. We demonstrate the possibility of controlling the degree of structural perfection of the evaporated films even at a condensation rate $\sim 10^{10}$ Å/sec. Films with the structure of a mosaic single crystal have been obtained.

The possibility of obtaining polycrystalline films of superconducting compounds by laser evaporation has been discussed in a number of papers.[1–3] However, we know of no publication devoted to epitaxial semiconducting films obtained with the aid of a laser.

We investigated the structure of thin films deposited with the aid of a Q-switched laser. The targets were samples of Bi_2Te_3. The substrates were freshly cleaved natural rock salt and mica (muscovite) plates. The substrate temperature t_s ranged from 20 to 350 °C. The



Electron diffraction patterns obtained from Bi_2Te_3 films deposited on NaCl at different substrate temperatures: 1) 20 °C, 2) 150 °C, 3) 250 °C, 4, 5) 300—350 °C, 6) electron diffraction pattern obtained from Bi_2Te_3 film deposited on mica at 350 °C.

pressure in the vacuum chamber was kept at the level $\sim 10^{-5}$ mm Hg. The radiation flux density on the target surface was $\sim 10^9$ W/cm^2. The substrates were located at a distance 25 mm from the target. The thickness of the film obtained from one radiation pulse was several hundred Angstroms. The films detached from the salt and from the mica were investigated by transmission electron diffraction in the EG-100A electronograph.

Figures 1—5 show electron diffraction patterns of thin films deposited on NaCl at different substrate temperatures. At $t_s = 20$ °C, the evaporated Bi_2Te_3 films have a finely-dispersed polycrystalline structure (Fig. 1). The first symptoms of a texture appear at $t_s = 150$ °C. The Bi_2Te_3 crystallites are ordered in the aximuthal direction and their {10. 5} planes are parallel to the substrate plane (Fig. 2). With further rise of the substrate temperature there is observed, in addition to an improvement in the film structure, also the appearance of an orientation {00. 1}Bi_2Te_3 ∥ (100)NaCl, which gradually crowds out the {10. 5} orientation. Heating the substrate to 250 °C makes it possible to obtain an epitaxial Bi_2Te_3 film oriented with the basal plane of the hexagonal lattice parallel to the substrate plane (Fig. 3).

In the region $t_s = 300—350$ °C there is again observed a competition between the two types of orientation {10. 5} and {00. 1}.

Point reflections correspond to either of the orientations are present in equal degree in most electron diffraction patterns (Fig. 4).

In individual cases it is possible to obtain in the indicated temperature range films with only one type of orientation {10. 5} (Fig. 5). The cubic grid of bright point reflections shows that the deposited film has the structure of a mosaic single crystal with a block disorientation on the order of several degrees. The competition of the two types of orientation is apparently due to the existence of two principal factors that determine the formation of the structure of the evaporated films, namely the influence of the potential relief of the NaCl substrate surface, which leads to the formation of a pseudocubic orientation {10. 5}Bi_2Te_3 ∥ (100)NaCl, and the anisotropy of the growth rate of the Bi_2Te_3 microcrystals, which contributes to formation of a predominant {00. 1} orientation.

The general rule that the film structure improves with increasing temperature remains in force also in the case of evaporation on mica. Owing to the similarity in the symmetry of the Bi_2Te_3 crystal lattices and of mica, only one type of orientation, {00. 1}, is observed. The most perfect epitaxial films were obtained at 350 °C (Fig. 6).

This raises the question whether the good orientation of the films is a consequence of annealing of the laser condensate as a result of the increased substrate temperature. A control experiment was performed. A Bi_2Te_3 film evaporated on mica at $t_s = 20$ °C was heated to 350 °C and annealed for a time equal to that usually consumed in the experiment with evaporation on the heated substrates. After annealing, this film had a finely-dispersed structure consisting of randomly oriented grains. At the same time, the film deposited on a substrate heated to 350 °C had a clearly pronounced orientation. Thus, the orientation of the film is produced precisely at the instant of condensation of the material.

It appears that the epitaxial growth of thin films by laser evaporation is aided by the appreciable energy excitation of the atoms of the condensed vapor. The atoms acquire the excitation energy needed to produce the crystallization chain reaction. [4] It is this precisely which explains the 100—150 °C decrease in the epitaxy temperature for the {00. 1} orientation on NaCl in comparison with the results obtained for Bi_2Te_3 films by ordinary methods. [5] In addition, under conditions when films are produced with the aid of a laser, there is a high degree of supersaturation, when the nucleus of the critical dimension can be an individual atom, and this should affect favorably the initial stages of the growth. [6] At the same time, our investigation shows that even at sputtering rates $10^9—10^{10}$ Å/sec the substrate temperature remains one of the most parameters of the condensation.

[1] H. M. Smith and A. F. Turner, Appl. Optics 4, 147 (1965).
[2] P. D. Lavitsanos and W. E. Sauer, J. Electrochem. Soc. 115, 109 (1968).
[3] V. S. Ban and D. A. Kramer, J. Mater. Sci. 5, 978 (1970).
[4] V. I. Petrosyan and E. I. Dagman, in: Problemy épitaskii poluprovodnikovykh plenok (Problems of Epitaxy of Semiconducting Films), Nauka, Novosibirsk (1973), p. 173.
[5] M. H. Francombe *et al.*, transl. in: Monokristallicheskie plenki (Single-Crystal Films), Mir, 1966, p. 136.
[6] T. N. Rodin and D. Walton, *ibid.*, p. 51.