Fabrication of Bi$_2$Te$_3$ films on the surface of silica optical fibres by MOCVD

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Abstract. Crystalline 2D bismuth and antimony chalcogenides, as well as graphene, can successively operate as saturable absorbers in various schemes of passively mode-locked fibre lasers. An attractive benefit of these saturable absorbers is their power to effectively operate at different wavelengths in the wideband from 1 to 2 microns. However, the problem is how to provide a reliable interaction between light in a fibre and the absorber. The main disadvantage of a standard solution to the problem essentially is to use exfoliated flakes dissolved in a coupling agent, which deposits additional heat that negatively affects the absorber. In the present research, thin crystalline films of a narrow-band semiconductor Bi$_2$Te$_3$ were deposited directly on silica optical fibres by means of metal-organic chemical vapour deposition (MOCVD). A ZnTe buffer layer was deposited first in a single growth run, providing the necessary condition for better adhesion of bismuth telluride film to the silica surface. Two types of fibre coatings were prepared and tested: the coating upon the cleaved end of the fibre and the one upon the lateral surface of the light-guiding fibre core. In the latter case, prior to deposition a fibre section of about 1 cm in length was uniformly thinned via chemical etching to a diameter of about 20 microns. Reflection and transmission of the growing films were monitored in situ during the deposition.

1. Introduction
Saturable absorbers based on atomically thin crystalline films of bismuth and antimony chalcogenides are used in the 1–2 μm wavelength range [1] despite the fact that the width of a forbidden band of these narrow-bandgap semiconductors does not fit the energy of photons in the wavelength range mentioned. This is possible due to the peculiarity of band structure and the optical absorption spectrum of thin films under consideration, which subjected to change under the impact of strong optical fields [2].

In practice, the manufacture of this type of saturable absorber is performed by mixing suspensions of nano-flakes exfoliated from the corresponding single crystal with a binding polymeric agent [3]. While relatively simple, this procedure results in the inevitable dispersion of flake sizes and the impairment of polymer-crystal interface states on the saturated absorber characteristics. In addition, high optical power density generates significant heat, which can lead to irreversible changes in the optical properties of an absorber.

An alternative way is the deposition of a thin semiconductor absorbing film directly on the surface of an optical waveguide. There are various technological methods suitable for this task ranging from molecular-beam epitaxy [4] to laser ablation [5] and magnetron sputtering [6]. Among them, we can highlight film deposition by metal-organic chemical vapour deposition (MOCVD) [7]. This process
does not require ultra-high vacuum, allows the obtainment of homogeneous films, and easily vary their composition in a single deposition run.

In this paper, we present the results of the first application of MOCVD to the deposition of Bi$_2$Te$_3$ films on the surfaces of a silica optical fibre.

2. Experimental

To obtain the thin-film coatings on a fibre, we used the MOCVD process outlined in [8]. The deposition took place in a horizontal tubular reactor heated by a resistance oven 10 cm in length to a temperature of 420–445 °C in the atmospheric pressure hydrogen flow. Trimethylbismuth (BiMe$_3$), diethyltellurium (Et$_2$Te) and diethylzinc (ZnEt$_2$) served as the precursors. The first two were used to deposit the Bi$_2$Te$_3$ absorbing film and the final one was given to obtain the ZnTe buffer and protective (top) layers. The 5–10 nm thick ZnTe buffer layer terminates open chemical bonds on the silica surface to strengthen the adhesion of the growing Bi$_2$Te$_3$ film to the surface.

Two types of silica fibre surfaces served as substrates for the deposition of films in our experiments. The first one was the cleaved end of a fibre. The second one was a lateral surface of a tapered section of standard single mode (SMF28) fibre. For taper manufacturing, the fibre was released from the polymer protective coating at a distance of 0.3–2 cm and placed in an etchant, the recipe of which is given in [9]. The diameter of the protection-free section of the fibre uniformly scaled down from 125 µm to approximately 20 µm during 100 min at a temperature of 27 °C. The fibre segments that were free of the protective polymer coating (12–15 cm in length) and accordingly prepared for deposition were housed in a hermetically sealed MOCVD reactor. Through the exteriorized fibre ends, one can continuously record changes in transmission and reflection spectra during the film growth on the fibre surfaces.

3. Results and discussion.

For deposition of the Bi$_2$Te$_3$ absorbing film, we used BiMe$_3$ at a partial pressure of $3 \times 10^{-5}$ ATM and a 15-fold excess of tellurium in the vapour phase. A rather high mass flow of bismuth is necessary for a high-rate deposition. This step turned out to be a mandatory requirement for the formation of a thin film uniform coat.

Under these deposition conditions, the necessary (10–40%) change of the reflectivity for the cleaved fibre end due to film deposition took place in 3–13 sec. The EDX analysis indicated the stoichiometry of the deposited Bi$_2$Te$_3$ film. The Raman spectra of the obtained thin films in addition to vibration modes of Bi$_2$Te$_3$ contained intense LO modes of the ZnTe buffer layer. The growth of the taper films caused a decrease in fibre transmission during the first 7–10 seconds of deposition. The final transmittance depended on both taper diameter and length.

![Fig. 1 a), b) - SEM and c) - AFM images of fiber taper coated by a thick crystalline Bi$_2$Te$_3$ layer via MOCVD. Deposition time of the Bi$_2$Te$_3$ film amounts to 250 sec.](image-url)
Figs. 1-a and -b show SEM images of the central part of the tapered fiber covered by a thick Bi$_2$Te$_3$ layer. The surface of this coating consists of large-size nano-flakes randomly oriented on the lateral surface of the fibre (Fig. 1c).

**Conclusion.**
The MOCVD technology has been employed for coating the cleaved ends of an optical fibre and/or lateral surface of the light-guiding core with a Bi$_2$Te$_3$ thin film saturable absorber. The developed technology is of immediate interest for the engineering of passively mode-locked fibres with a wavelength range of 1–2 µm and waveguide lasers.

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