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Complex crystallization behavior and oriented layer growth of amorphous MoTe$_2$ nanofilms on transition-metal substrates

© P.N. Yakushev[1], V.A. Bershtein[1], A.V. Kolobov[2]

[1] Ioffe Institute,
St. Petersburg, Russia
[2] Herzen State Pedagogical University of Russia,
St. Petersburg, Russia

E-mail: yak@pav.ioffe.ru

Transition metal dichalcogenides have found wide application in various fields of electronics (spintronics, optoelectronics, memory devices), as two-dimensional semiconductors in the form of thin crystalline films. One of the methods for their production is crystallization in the solid state from the amorphous phase onto various substrates. In this work, DSC measurements show that the MoTe$_2$ nanolayer deposited on different substrates Ta, Al, W, Mo) is in different structural states: amorphous, partially crystalline or completely crystalline. Their glass transition temperatures, crystallization ranges and enthalpies were found to vary depending on the substrate This means that whatever the reason for the observed differences, results obtained on one substrate cannot be transferred when the substrate material is changed.

1. Introduction

A great interest in the study of 2D-semiconductors emerged after considerable success was achieved in the analysis of the properties of 2D-systems based on graphene. One of the promising classes of such materials are transition-metal dichalcogenides (TMDCs) [1] with the common formula MX_2 ($M = $ Mo, W, and $X = $ S, Se, Te). These materials have laminar structure, where sandwiches X-M-X, often called monolayers, are held together with low Van der Waals forces. The interest in these materials recovered around 10 years ago, when it was found that the structure of the band gap MoS$_2$ changed from the indirect one in volume form to direct one in monolayer limit [2]. Unique properties of 2D TMDCs were found, such as extremely high energies of exciton bonds [3], spin-valley bond type [4] etc. Moreover, MoTe$_2$ may exist in various stable polymorphous forms, semiconductor and metal ones, where transitions between various structures may be very quick, in the subpicosecond time scale [5,6]. Multiple and diverse devices were demonstrated on the basis of several layers and monolayer of TMDCs — from field transistors to lasers, from memory cells to biomedical applications. In most cases the devices were made of monolayer TMDCs, manually scaled from the array. However, such approach is not suitable for industrial applications, which require a simple and industry-friendly method to manufacture thin crystals of TMDCs. One of such methods is crystallization of nanofilms from amorphous phase. An amorphous solid body is isotropic (3D), while TMDCs in crystalline form are lamellar, 2D-materials. Therefore, when TMDC nanofilms are crystallized, the lattice size changes, i.e. transition of 3D-2D.

This transition is illustrated in Figure 1, where a „shot" of molecular-dynamic state of amorphous MoTe$_2$ is compared to stable 2H phase [1]. It is well seen that 3D-amorphous structure turned into 2D-crystalline phase with triple layers Te-Mo-Te.

2. Experiment

In this paper we experimentally studied the process of crystallization of nanolayers MoTe$_2$ on various substrates using differential scanning calorimetry (DSC). Specimens were made by method of magnetron sputtering of a target with composition MoTe$_2$ and presented films with thickness of 100 nm, applied on both sides of the foil with thickness of $20-25$ mkm from four different metals: Al, Ta, Mo and W. In case of foil Ta, Mo and W a 50 nm nanolayer SiO$_2$ was additionally applied on top of MoTe$_2$ to prevent oxidation. Note that three of these metals (Mo, W and Ta) form TMDC, besides one of them (Mo) is a transitional metal in the studied film.

DSC measurements were carried out on calorimeter DSC 6300 (Seiko Instruments, Japan) at heating rate 10 °/min in atmosphere N$_2$; the nitrogen flux rate was 40 ml/min. Cooling rate after scanning was 20 °/min. Calibration of the temperature scale and enthalpy effects was carried out according to indium ($T_m = 156.6$°C, $\Delta H_m = 28.6$ J/g) and zinc ($T_m = 419.6$°C, $\Delta H_m = 107.5$ J/g) standards.
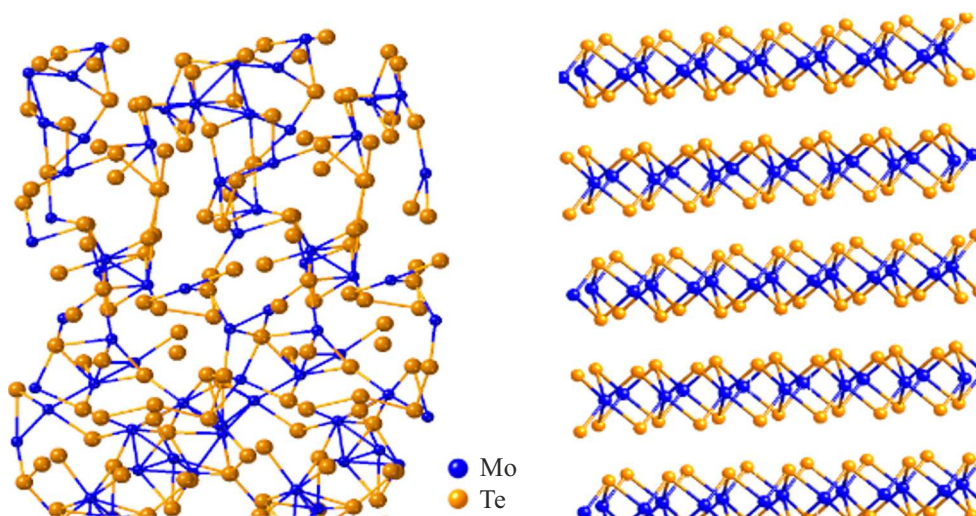
Figure 1. 3D-amorphous phase (on the left) and 2D-crystalline phase $MoTe_2$.

Characteristics of DSC in nanolayers $MoTe_2$ on different substrates: initial state and parameters of crystallization

Material of substrate (foil)	Mass $MoTe_2$ on substrate, mg	T_g, °C	Temperature range of crystallization, °C	T_{cr}^{max}, °C	Enthalpy of crystallization ΔH_{cr}, kJ/g	Initial state $MoTe_2$ on substrate
Ta	1.8	333	355−470 428−490 624−807	400 470 680	18.6 3.8 3.7	Amorphous
W	1.6	450	468−800	494 680	3.8	Partially crystalline
Al	1.2	468	475−560	495	0.5	
Mo	1.8	−	−	−	−	Crystalline

Every studied specimen presented the stack of circles with diameter of 5 mm, cut from foil and coated on both sides by nanolayers $MoTe_2$. Depending on substrate material the total mass of the specimen varied from 250 to 500 mg, whereas mass $MoTe_2$ was 1−2 mg (see table). This stack was placed in a ceramic capsule with internal diameter of 6 mm. As a reference, a similar capsule was used with a stack of metal circles of the same mass cut from the same foil, but without nanolayers $MoTe_2$ and SiO_2. Accuracy of glass transition T_g and crystallization T_{cr} temperatures detection was 1−2°, while enthalpies of crystallization, ΔH_{cr}, could be defined with accuracy of up to 20% only due to the limited accuracy of specimen $MoTe_2$ mass detection. DSC curves were obtained in the temperature range from 200 to 900°C in case of Ta, W and Mo substrates, and in the range from 200 to 600°C in case of Al substrate.

3. Results and discussion

Figure 2, *a, b, c* presents DSC curves for nanolayers $MoTe_2$ on different substrates (foils), produced in the temperature range from 200 to 600−900°C. Crystallization ranges, maximum values T_g and T_{cr}, and enthalpies of crystallization ΔH_{cr}, obtained as a result of measurements, are given in the table.

The most important result of these measurements is drastically different thermal behavior of nanolayers $MoTe_2$, provided for by strong effect of substrate material at structural condition of deposited nanolayers. In case of Ta substrate, obviously, amorphous nanolayers were deposited, since low $T_g = 333$°C, maximal heat capacity step and high crystallization enthalpy ΔH_{cr} were recorded in this transition. Besides, three areas of crystallization process are observed at temperatures from 355 to 807°C (Figure 2, *b*, table). All these features disappeared on a DSC curve during the second scanning after heating to 900°C and cooling of the specimen, which indicates that they are related to the irreversible crystallization process.

Figure 2, *a* shows a DSC curve obtained for nanolayers $MoTe_2$ on Al substrate. In this case nanolayers $MoTe_2$ were not coated by nanolayer SiO_2, and certain Te allocation could have taken place [7]. This is indicated by manifestation of small exothermic and endothermic peaks
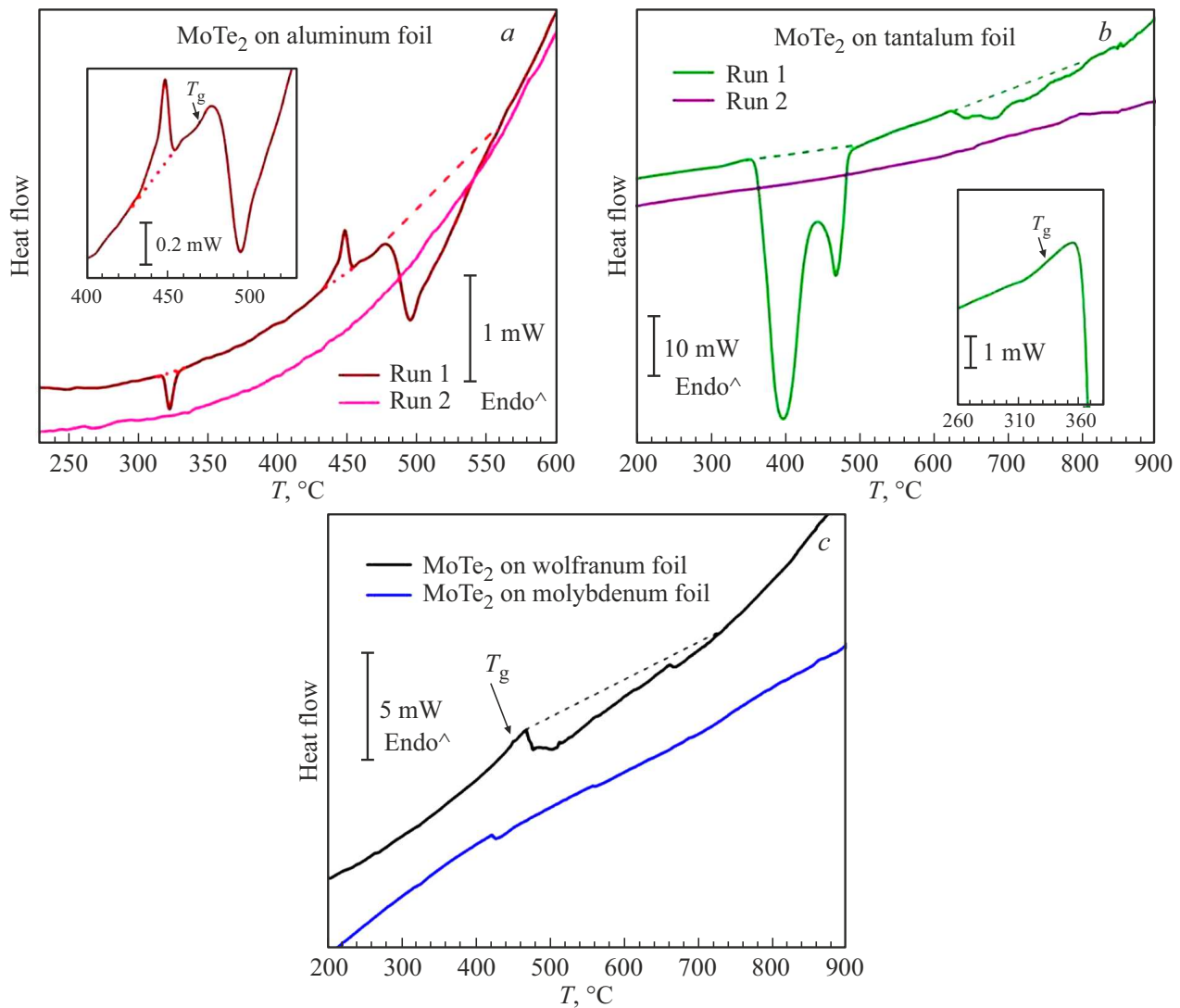
Figure 2. DSC curves of nanolayers MoTe$_2$ (with thickness of 100 nm) during the first and second scanning on aluminum (a), tantalum (b) and during the first scanning on tungsten and molybdenum foils (c).

at 323 and 445°C, accordingly, which may be referred to crystallization and melting of Te. Low enthalpy of crystallization ΔH_{cr} in this case indicates mixed amorphous-crystalline state of nanolayers MoTe$_2$, with the high degree of crystallinity already in the initial nanolayer prior to thermal treatment. A heat capacity step at $T_g = 468°$C is also 10 times smaller than for nanolayers MoTe$_2$, deposited on Ta substrate. Since „residual" crystallization of nanolayers MoTe$_2$ on Al-foil occurs at much higher temperatures, starting from 475°C.

A rather close initial state of partially crystallized nanolayers MoTe$_2$ is observed on W foil, even though when heated to 728°C their residual crystallization occurs (table). Finally, nanolayers MoTe$_2$ on Mo substrate demonstrated no significant features when heated; the DSC curve showed no exothermic or endothermic effects even upon the first scanning, which means that they were fully crystalline already after deposition (Figure 2, c).

4. Conclusion

Therefore, we found great effect of substrate material at structural state of deposited nanolayers MoTe$_2$. It seems that the growth of oriented films is related to the transitional metal atoms and chalcogen atoms affinity, when upon sputtering the surface is first passivated by tellurium atoms, and then the film further grows in the layer-by-layer mode. Note that this process reminds the process of self-organized growth of films in the mode of Van der Waals epitaxy on substrates of certain compositions [8]. Besides, the obtained data indicate that the results produced on one substrate could not be used upon changing the substrate material

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Conflict of interest

The authors declare that they have no conflict of interest.

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