Reversible semiconductor-semimetal phase transition in monolayer CVD-grown $MoTe_2$

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Monolayer molybdenum ditelluride ($MoTe_2$) is known to exist in two structural polymorphs: semiconductive (1H) and semimetallic (1T'), with extremely low ground state energy difference (30 meV/f.u.). 1H-$MoTe_2$ is a semiconductor with direct optical band gap of 1.1 eV [1], while 1T'-$MoTe_2$ is a semimetal with non-trivial topological states [2] and superconductor [3]. Such properties make $MoTe_2$ an attractive material for phase-change devices and low contact resistance semiconductor-semimetal circuitry for micro- and optoelectronics. Achieving controllable and reversible phase transformation between these two phases shall impact the development of $MoTe_2$-based electronic devices. In this work, we investigate phase transition for chemical vapor deposition (CVD) grown monolayer 1T' and 1H $MoTe_2$ upon annealing in ultra-high-vacuum (UHV). In all experiments $MoTe_2$ was encapsulated with monolayer CVD graphene and we performed ex-situ UHV annealing followed by Raman spectroscopy measurements. Atomic structure and heterointerfaces of 1H-1T' phases were examined by HRTEM microscopy. CVD-grown monolayer 1T'-$MoTe_2$ was observed to locally transform into 1H phase after UHV annealing at 800 °C with a transition rate of ~ 100 nm/min while nearly complete conversion was observed upon annealing at 900°C for 15 minutes. The quality of the realized 1H phase could be improved by using an additional layer of graphene encapsulation (i.e., bilayer graphene), by reducing annealing temperature and increasing annealing time. CVD-grown monolayer 1H-$MoTe_2$ was converted into 1T'-$MoTe_2$ at temperatures higher than 1090 °C and we observed phase reversion (i.e., 1T' to 1H) by subsequent annealing at 900 °C. Theory predicts a 1H to 1T' transition temperature as low as 417 °C [4], while previous experiments observed such phase transition at 1075 °C in exfoliated $MoTe_2$ flakes encapsulated with few-layer hBN, but no reversion was reported until now [5]. We perform DFT simulations and discuss possible explanations of discrepancies between experimental data and theoretical prediction. Our experiments confirm the metastable nature of the 1T' phase and demonstrate the possibility of a reversible 1H-1T' transformation in CVD-grown $MoTe_2$.

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