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Tempered growth of metastable polymorphs on amorphous substrates with seed layers

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Metastable inorganic materials with unique properties are important in many practical applications, but their synthesis is often challenging. In physics, epitaxial stabilization, also known as pseudomorphic growth, has been used to synthesize metastable polymorphs, but usually only as very thin films, and on expensive single crystal substrates. In chemistry, templated growth of inorganic solid state materials on self-assembled monolayers of organic molecules has been reported. Bridging these two fields, here we show that synthesis of metastable polymorphs is possible up to large film thickness, on amorphous substrates covered with thin inorganic seed layers that serve as templates. Stabilization of a 500 nm thick metastable wurtzite (WZ) MnTe film by a 5 nm thin ZnTe seed layer sputtered on amorphous glass substrates is experimentally demonstrated. Theoretical calculations explain this experimental observation by the small WZ polymorph energy compared to the ground state nickeline (NC) structure of MnTe, and a large lattice constant difference of the two. The resulting metastable WZ-MnTe polymorph exhibits a wide band gap of 2.7 eV and a low hole density of $10^{12} \text{cm}^{-3}$, relevant to optoelectronic applications. These properties are in sharp contrast to the narrow-bandgap highly-doped NC-MnTe with 1.3 eV band gap and $10^{19} \text{cm}^{-3}$ hole density. The difference in hole density is due to the calculated difference in the formation energy of manganese vacancy acceptor defects. Overall, these results suggest that templated growth on amorphous substrates with seed layers can be used to synthesize metastable polymorphs of other materials, without the need for expensive single crystal substrates.
I. INTRODUCTION

Metastable materials are ubiquitous in our lives, as they are used across a broad range of practical applications. Examples among inorganic solids include the diamond polymorph of carbon, austenitic steel alloys, GaInP₂ compounds in multi-junction photovoltaics, and amorphous glass in building windows. One type of metastable material of particular relevance to this paper is polymorphs – materials with the same composition but different crystal structure than their stable counterparts. Metastable polymorphs are important for technological applications because they can have completely different properties than their thermodynamically stable ground states. For example, it has been theoretically predicted that the archetypical wide band gap n-type semiconductor ZnO can be doped p-type using Li, if its rock salt polymorph rather than wurtzite ground state is stabilized. [1] This is important because wide band gap (WBG) p-type semiconductors are desirable for (opto-)electronic devices, such as solar cells, thin film transistors, photodetectors, and light emitting diodes, [2–4] but their p-type doping is often difficult to achieve. [5–7] Metastable polymorphs are also interesting from the point of view of synthesis science. Understanding how to synthesize polymorphs in a controlled way can dramatically increase the number of possible materials that can be used for the aforementioned technologies and many other practical applications.

One common approach to synthesize metastable polymorphs in thin film form is epitaxial growth [8] also known as “pseudomorphic stabilization”. [9] This approach is based on the idea that the crystal structure of the film grown on the substrate is determined by the total free energy of the film/substrate system, which includes bulk and interface components. Such epitaxial growth has been used in the past for many materials, for example to engineer functionality into complex oxides grown using molecular beam epitaxy (MBE) [10] by tuning of ferroelectric properties by strain energy [11] between single crystal substrates and thin films. As another example, films of high-energy rock salt polymorphs of GaN [12] and AlN [13] have been synthesized by epitaxial growth on TiN and MgO of up to 1 - 2 nm thickness. However, the broad use of this physical method for synthesis of metastable polymorphs in thin film form thus far has been limited by the use of expensive single crystal substrates, the complexity of MBE methods, and by the very small critical thickness of the films. A related chemical method for synthesis of metastable materials is templated growth from solution on self-assembled monolayers, with the resulting structure (e.g calcite, vaterite and aragonite polymorphs of CaCO₃)
controlled by selection of organic molecules. [14], [15]

Recently, we discovered that metastable wurtzite polymorph of MnTe (WZ-MnTe) can be stabilized on amorphous indium zinc oxide (a-IZO) coated glass. [16] Surprisingly, we found that the growth of WZ-MnTe on a-IZO was not limited to critical thickness and not influenced by work function of the substrate. We hypothesized that the WZ-MnTe stabilization may be due to the interdiffusion at the WZ-MnTe/a-IZO interface. However, it remained unclear whether the stabilization is due to *chemical alloying* and/or *structural templating* mechanisms. To investigate the *chemical alloying* mechanism, we synthesized Mn$_{1-x}$Zn$_x$Te on glass substrates and found that the WZ polymorph can be stabilized at $x > 0.08$–0.18 depending on growth temperature (300–400°C). [17] These experimental observations were theoretically explained by much larger mixing enthalpy of Mn$_{1-x}$Zn$_x$Te alloys in the NC compared to the WZ structure, similar to stabilization of “negative pressure” WZ polymorphs in MnSe$_{1-x}$Te$_x$ heterostructural alloys. [18] However, the properties of the metastable WZ-MnTe polymorph synthesized in these Mn$_{1-x}$Zn$_x$Te and MnSe$_{1-x}$Te$_x$ experiments were modified by inclusion of Zn or Se alloying constituents, so alternative synthesis routes to WZ-MnTe were desirable. In addition, a contribution of the *structural templating* mechanism to WZ-MnTe stabilization remained unknown.

Here we show that a metastable wurtzite (WZ) polymorph of manganese telluride (MnTe) can be synthesized using sputtering on amorphous substrates covered with ultrathin seed layers. Specifically, a ~500 nm thick WZ-MnTe is sputtered on a 5 nm thin ZnTe seed layer deposited on an amorphous fused silica substrate. The stabilization of the WZ phase is explained by the theoretical prediction of the polymorph energy difference as a function of lattice constant. The resulting WZ-MnTe metastable polymorph shows a wide 2.1 - 2.7 eV band gap and low $10^{12}$ cm$^{-3}$ hole density – considerably different from the 1.3 eV band gap and $10^{19}$ cm$^{-3}$ hole density of the thermodynamic ground-state nickeline (NC) structure. The drastic difference in electrical properties is explained by the >1 eV larger formation energy of acceptor-type manganese vacancies, determined using first principles defect calculations. Overall, these results demonstrate how templated growth on amorphous substrates with seed layers can be used to synthesize metastable polymorphs, and expand the range of known wide bandgap p-type materials for optoelectronic applications.
II. METHODS

Thin films reported in this work were deposited by a customized AJA combinatorial radio frequency sputtering system from 50.8-mm diameter ZnTe (99.99% purity) and MnTe (99.9%) targets tilted relative to the substrate. The stationary 50.8 × 50.8 × 1.6 mm amorphous fused silica substrates were used to avoid the influence of substrate crystal structure on the thin film growth. The working pressure was 1.3 mTorr with the ultra high purity Argon flow rate of 16 sccm. The chamber was pumped down to 1 × 10⁻⁶ Torr before deposition. The deposition rate of ZnTe decreased from 5 - 10 nm/min to 3 - 6 nm/min with increasing substrate temperature \(T_{\text{sub}}\), while that of MnTe was in the range of 2 - 5 nm/min regardless of temperature, as summarized in Table S1. These rates combined with 90-180 min deposition times resulted in 450-500 nm typical thicknesses of WZ MnTe films, and 300 min depositions led to 1260 nm thick films. More deposition details were described in our previous work. [17]

To characterize the samples, x-ray fluorescence (XRF, Fischerscope XDV-SDD) was utilized to determine the composition and the thickness with a 3-mm-diameter spot size, confirming the MnTe films to be stoichiometric withing the accuracy of the methods (0.1-1.0 at.%). X-ray diffraction was measured using Cu Kα radiation on a XRD, Brucker D8 with a 2D detector in approximate 2-theta geometry. Transmittance and reflectance were measured using a custom Ocean optics UV-Vis spectrometer system with wavelengths from 300 to 1000 nm, and used to determine optical absorption. Carrier concentration and Hall mobility as a function of temperature were determined from the magnitude and sign of the Hall voltage and from electrical resistivity, all measured using Lakeshore instrument (model 8425), under a magnetic field of 2 T. We note that low hole density and large surface depletion width for WZ-MnTe, as well as possible magnetic character of the MnTe mateirals, could have convoluted analysis of the Hall effect measurement results. SIMS was performed on a Cameca IMS-7f instrument using an oxygen primary ion beam at 10kV and a sample potential of 5kV with positive secondary ions. The cross-sectional TEM lamella of the 300 °C MnTe/ZnTe/SiO₂ sample was prepared in a FEI Nova dual beam and analyzed under conventional TEM conditions to assess the lattice spacings. The results were analyzed using custom COMB Igor analysis package for Igor Pro (https://www.combigor.com/), [19] and the raw data is available in the High Throughput Experimental Materials Database (https://htem.nrel.gov/). [20] Detailed characterization information can also be found in our previous work. [21]
The polymorph energies were calculated from first principles in Random Phase Approximation (RPA), with a variational optimization of the wavefunction that correctly recovers the Mn-d/Te-p hybridization of the MnTe polymorphs. [18] Defect calculations were performed using the projector augmented wave method implemented within the VASP code. [22], [23], [24], using the meta-GGA SCAN functional. [25] The results of our defect calculations using PBE+U [26], [27] with U = 3 eV applied to Mn₄ [28] are reported in the SM for reference. An energy cutoff of 800 eV and minimum k-point grid densities of ~1000 per reciprocal atom were employed in all calculations to achieve total energy convergence to 0.005 eV/atom. The defect calculations were performed on nickeline and wurtzite 72-atom supercells. To account for supercell finite-size effects in our calculations, we applied a correction scheme. [36] A linear scissor correction was applied to the results in Fig. 4 to align the VBM and CBM to the predicted GW bandgaps from https://materials.nrel.gov/

III. RESULTS AND DISCUSSION

A. Composition and Structure

The XRD patterns of the chemically stoichiometric MnTe/ZnTe/SiO₂ samples (MnTe on 5-nm ZnTe on a-SiO₂ substrate) and MnTe/SiO₂ control samples (MnTe on a-SiO₂ substrate) deposited at 300 and 400 °C, all with 440-500 nm thickness (Table S1), are shown in Figure 1(a). At 400 °C, only NC MnTe is observed regardless of the substrate, as expected because this is the lowest energy polymorph of MnTe. However, at 300 °C, the XRD peaks of the MnTe/ZnTe/a-SiO₂ samples can all be matched to the calculated WZ structure XRD reference pattern (Figure 1(a)), whereas MnTe/a-SiO₂ remains in the NC structure (Figure 1(a)). All the films are polycrystalline, with no single preferential orientation, suggesting that the substrate strain is fully relaxed. XRD for other deposition and annealing temperatures as well as ZnTe on a-SiO₂ is shown in Figure S1 in Supporting Materials (SM). [30] For the <300 °C MnTe depositions, some MnTe₂ phase impurity is formed, whereas at >300 °C MnTe forms in the NC structure. ZnTe remains in its ground state zinc blende (ZB) structure with preferential (111) orientation in 200 – 300 °C range, and above 500 °C it does not adhere to the substrate. The MnTe/ZnTe/SiO₂ sample deposited at 300 °C and annealed at 400 °C retained the WZ phase with negligible amount of NC phase (Figure S1).
Figure 1(b) summarizes the results of secondary ion mass spectrometry (SIMS) based on 250 nm MnTe/ZnTe/SiO₂ samples, showing the Mn and Zn signal intensity as a function of distance from the sample surface. For the samples deposited at both 300 and 400 °C, a small Zn signal close to the a-SiO₂ substrate (10-100 counts/second) is detected, but for the majority of the film no Zn signal is observed above the noise level (1-10 counts/second at depth < 200 nm), the same as for the MnTe samples. Complementary Auger Electron Spectroscopy (AES) depth profile measurements (<0.1-1.0% detection limit) did not find any oxygen or other major unintentional impurities in the bulk as shown in Figure S2. At both temperatures, it appears that the Zn depth profile in MnTe remains approximately the same, yet MnTe exhibits a totally different crystal structure: WZ at 300°C and NC at 400°C (Figure 1(a)). A cross-sectional microscopy image of the film/seed/substrate interface for the 300 °C MnTe/ZnTe/SiO₂ sample is shown in Figure S2, confirming the WZ phase based on the lattice constant. The presence of the seed layer in Figure 1(b) indicates that alloying through the thickness of the film is not responsible for the WZ phase stabilization observed here. In addition, the overall Zn content in both samples determined from XRF is <0.04 cat. at. %, which would lead to a mixture of NC and WZ phases according to our previous reports. [17] Thus, there must be a different mechanism responsible for stabilization of the WZ-MnTe polymorph.
Figure 1. (a) XRD patterns of 450-500 nm thick MnTe thin films on a-SiO$_2$ substrates as a function of temperature (300 °C vs 400 °C) and seed layer (ZnTe vs. none). (b) SIMS depth profiles of 250 nm thick MnTe/ZnTe/SiO$_2$ samples deposited at different temperature (300 °C vs 400 °C). These results suggest the stabilization of WZ structure at lower temperatures by templated growth.

**B. Stabilization mechanism**

To understand the stabilization of WZ-MnTe on the ZnTe seed layer, we calculated the bulk equation of state (energy vs. volume) for the two observed MnTe polymorphs WZ and NC (Figure 2(a)) from first principles in Random Phase Approximation (RPA) [18]. As shown in Figure 2(b), the WZ polymorph of MnTe would be stable if its energy ($E_{pm}^{WZ}$) is lower than the strain energy of the NC ground state structure ($E_{st}^{NC}$):

$$E_{pm}^{WZ} < E_{st}^{NC} + \Delta E_{if} + \Delta E_{sf}$$

(1)

where $\Delta E_{if} = E_{if}^{NC} - E_{if}^{WZ}$ and $\Delta E_{sf} = E_{sf}^{NC} - E_{sf}^{WZ}$ are differences in the interface and surface energies of the two polymorphs, which are typically smaller than the bulk energies (<100 meV/A$^2$). [31] The results of our calculations shown in Figure 2(a) indicate that the strain energy of the NC polymorph at the WZ equilibrium volume (1500 meV/at) is much larger than this polymorph energy difference (7 meV/at) at the respective equilibrium volumes ($V_{eq}$). Thus, we conclude that when MnTe is deposited on the ZnTe seed layer, it minimizes the overall energy by adopting the WZ crystal structure, which is close in energy to the ground state NC crystal structure. A detailed derivation of Eq.1 and a schematic corresponding to the general case (Figure S3) are presented in SM.


Figure 2. (a) Calculated bulk equation of state for the WZ and NC polymorphs of MnTe. The polymorph energies are similar, but the strain energies are different. (b) Schematic illustration of the total energy of a MnTe thin film grown on a thin ZnTe seed deposited on an a-SiO$_2$ substrate. The WZ-MnTe can be stabilized if the WZ polymorph energy is smaller than the NC strain energy.

Polymorph stabilization has been previously observed for metastable ZB-MgS films deposited on GaAs crystals, [32] and for various metastable oxides and nitrides [8], [12] grown on single crystal substrates, up to a small critical thickness, and using complex molecular beam epitaxy (MBE) methods. The important differences between this study and all these prior thin film reports are the (a) thick 500 nm metastable WZ-MnTe layers, (b) deposited using a simple sputtering technique, (c) on 5 nm thin ZnTe seed layers, (d) on inexpensive amorphous glass substrates. Such templated growth opens up a huge new space for stabilization of high-energy polymorphs in materials systems, where lattice matched single crystal substrates are not...
available and complex deposition methods are not feasible, and where thick films are required for practical applications. This discovery also highlights the importance of emerging tools for high-throughput studies of metastable materials, such as combinatorial substrate epitaxy. [33]

C. Optical and electrical properties

One of the distinguishing features of the WZ polymorph of MnTe is its wide bandgap relative to the NC polymorph of MnTe. The transmittance spectrum, corrected by the reflectance spectrum to avoid interference fringes, of WZ and NC MnTe deposited at 300 °C is shown in Figure 3(a). WZ-MnTe has a corrected transmittance of 90% in the wavelength range of 600 to 1000 nm, in contrast to the nearly opaque NC-MnTe ground state structure. The corresponding absorption thresholds determined from the logarithmic plots of the absorption coefficient are approximately 2.7 eV for WZ-MnTe (with some sub-threshold absorption) and 1.3 eV for NC-MnTe. This difference is consistent with the theoretically calculated values of band gaps reported at https://materials.nrel.gov/. Absorption coefficient plots of MnTe samples grown on amorphous fused silica with/without a ZnTe seed layer are provided in Figure S4. Not surprisingly, phase-pure WZ MnTe exhibits a wide band gap (2.7 eV) while the others have lower optical absorption onsets of <1.3 eV due to the NC-MnTe and MnTe2 impurities.

The difference in the band gaps of WZ and NC MnTe also correlates with the dramatic change in the electrical properties of these semiconductors. Figure 3(b) summarizes the preliminary carrier concentration and mobility measurements by Hall effect, as a function of temperatures for NC-MnTe and WZ-MnTe samples. Both samples show the positive sign of the Hall coefficient, indicating that the materials are p-type semiconductors. The WZ-MnTe has a much lower hole concentration (~10^{12} cm^{-3}) compared to NC-MnTe (~10^{19} cm^{-3}). It is unlikely that extrinsic impurities such as O and C lead to such huge difference in hole concentration, since they were not observed by AES (Figure S2), and since the synthesis conditions for both polymorphs were similar. The low hole concentration along with the wide band gap is beneficial for application as channel layer in thin film transistors. The WZ-MnTe hole mobility value for our sputtered small-grain polycrystalline samples is ~1.4 cm^2/ Vs, which is comparable to NC-MnTe and to other known wide bandgap p-type semiconductors used in thin film transistors. We also note that the hole mobility is likely to be considerably higher for the WZ-MnTe films with larger grains because the calculated hole effective mass for this material is quite low. [17]
Figure 3. (a) Transmittance vs. wavelength, and absorption vs. energy for WZ and NC polymorphs of MnTe. The WZ phase has wider bandgap than the NC phase. (b) Hall concentration and mobility of WZ-MnTe and NC-MnTe as a function of measurement temperature. The WZ phase has a much lower carrier concentration compared to the NC phase.

D. Defect calculations

The measured dramatic difference in the hole concentration of NC and WZ polymorphs of MnTe can be explained by the difference in the native point defect concentrations. Theoretical calculations shown in Figure 4 suggest that WZ-MnTe has an ~1 eV higher formation enthalpy of acceptor-type manganese vacancy (V_{Mn}) defects compared to NC-MnTe, which is the main difference in defects physics of the WZ and NC polymorphs. For both polymorphs, the Mn_{Te} ambipolar antisite defects and the V_{Te} donors have similar energies to V_{Mn} acceptors, for the Fermi level (E_{F}) positions close to the valence band. Thus a comparable number of donors may be present at this equilibrium E_{F}, so overall the material acts as a compensated semiconductor. Other possible defects (e.g. Te_{Mn}) are higher in energy, so they don’t significantly contribute to the charge balance. Defect formation energies using the SCAN and PBE+U functionals for NC and WZ MnTe are also reported in Figure S5 in SM. Overall, these theoretical predictions are
consistent with the experimental observation that the hole concentration in WZ-MnTe is several orders of magnitude below that in NC-MnTe.

Figure 4. Defect formation energies under Mn-rich conditions, as a function of Fermi level for MnTe in (a) nickeline and (b) wurtzite crystal structures. The WZ-MnTe is expected to have a lower density of free holes based on the higher energy of the manganese vacancy acceptor defects compared to NC-MnTe.

IV. CONCLUSIONS

In the future, WZ-MnTe polymorph with wide bandgap and low doping can be applied as a channel layer in transistors used for transparent electronics. [34] The low doping levels are desirable for achieving low off-state current density and hence high on/off ratios, and the wide band gap implies transparency in the visible region of the optical spectrum. In addition to these two basic properties, the channel layer must also possess low densities of tail states near the band edges and trap states in the gap, [35] as well as have suitable band offsets with the gate insulator material. Further calculations and experiments to determine these properties are warranted. Other potential future applications of WZ-MnTe include intrinsic layers for photodetectors because its low carrier density would lead to high photosensitivity, and because its wide band gap would lead to low thermal noise for reliable room temperature operation. [36] For both transistors and
photodetectors based on WZ-MnTe, NC-MnTe can be used as p-type contact without the need for extrinsic doping. This may be possible to implement by depositing NC-MnTe at 400 °C (Figure 1), since at this temperature the underlying WZ-MnTe deposited at 300 °C would remain stable (Figure S1).

In summary, we have demonstrated the grow of thick metastable materials using a simple sputtering technique on amorphous glass substrates covered with thin seed layers. A metastable wurtzite polymorph of MnTe with 500 nm thickness was sputtered on a 5 nm thick ZnTe layer at 300 °C. The templated growth was theoretically explained by small differences in the bulk polymorph energies and large differences in the interface strain energies. Compared with the ground state nickeline MnTe structure with a 1.3 eV band gap and 10^{19} cm^{-3} hole density, the metastable wurtzite polymorph shows a wide 2.7 eV bandgap and low 10^{12} cm^{-3} hole concentration, with a reasonable mobility of 1.4 cm^{2}/Vs for p-type nanocrystalline thin films. The lower doping level of WZ-MnTe relative to NC-MnTe is explained by the higher formation energy of acceptor-type V_{Mn} defects in this metastable polymorph. In contrast to the ground state NC structure, this WZ polymorph is an attractive candidate for wide bandgap (opto-)electronic devices such as thin film transistors or photodetectors. Overall this work demonstrates an example of how new properties can be achieved in known materials by synthesis of their metastable polymorphs.

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