

Selective Deposition of Phase Change Materials by Chemical Vapor Deposition and Electrodeposition

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ABSTRACT

We report selective deposition methods for phase change materials by chemical vapor deposition (CVD) and electrodeposition. Firstly, high selective deposition of SnSe₂ and Bi₂Te₃ films on TiN is observed in low pressure CVD on photolithographically patterned SiO₂/TiN substrates by single source precursors. Secondly, a non-aqueous electrochemical system for the electrodeposition of high-purity elemental Bi, Sb, Se and Te is described. This system enables the deposition of binary and ternary phase change materials. The deposition and characterization of Sb₂Te₃ by this system is presented.

Key words: Phase change materials, selective deposition, chemical vapor deposition, electrodeposition.

1. INTRODUCTION

Phase change random access memory is considered as one of the most promising candidates for next-generation non-volatile solid-state memory due to its outstanding performances, such as non-volatility, high scalability, high speed, low power, low cost, and compatibility with CMOS process [1]. As the cell size scales down, the issue of thermal cross-talk between adjacent cells has been raised. Growth of the entire device inside a contact hole is hence more favorable as it could reduce the thermal cross-talk between cells and simultaneously reduce the currents required for SET and RESET operations. However, the conventional deposition of phase change materials by sputtering does not allow selective deposition and is unable to uniformly fill small holes. Hence new deposition technologies are investigated.

CVD is a widely used deposition process in industry for semiconductor alloys, with most processes using dual or multiple sources. While substrate selective CVD of semiconductors is known and can lead to deposition of different film morphologies, there are no examples reported for area selective CVD via single source reagents. Electrodeposition of compound semiconductor materials has also attracted recent attention [2]. The bottom-up approach of electrodeposition makes it a promising approach to depositing materials selectively into conductive nano scale holes [3]. However, the requirement of solubility in water limits the exploitation to a small range of binary and ternary compounds, and deposition of elements such as Germanium is very difficult in these systems.

In this paper, we report two novel approaches to achieve area selective deposition of phase change materials. Firstly, single precursor low pressure chemical vapor deposition (LPCVD) of SnSe₂ and Bi₂Te₃ phase change materials is presented with both depositions showing selective deposition behavior on TiN contact holes within photolithographically patterned substrates (SiO₂/TiN). Secondly, the non-aqueous electrodeposition of elemental Bi, Sb, Se and Te is presented together with the deposition of phase change Sb₂Te₃ on TiN contact holes. The use of the non-aqueous system allows the expand the range of the electrochemical system which is expected to allow the incorporation of germanium into the Sb₂Te₃ films and the low surface tension of the non-aqueous electrolyte will also allow the deposition into nano scale holes.

2. EXPERIMENTAL SECTION

Substrate: The patterned substrates were fabricated for selective deposition for both LPCVD and electrodeposition. The fabrication process is shown in Fig.1(a). SiO₂ and TiN films were deposited by medium frequency dual

magnetron sputtering. A photolithographic process was then applied to pattern structures (holes and squares) with sizes ranging from 1 μm to 100 μm . This was followed by a reactive-ion etching of SiO_2 to form the hole structure as shown in the Fig. 1(b).

LPCVD: $[\text{SnCl}_4\{\text{Bu}^n\text{Se}(\text{CH}_2)_n\text{Se}^n\text{Bu}\}]$ ($n = 2$ or 3) and $[\text{BiCl}_3(\text{Te}^n\text{Bu}_2)_3]$ single precursors were prepared for SnSe_2 and Bi_2Te_3 , respectively. In both CVD experiments, the reagent and substrates were placed end to end into a closed-end silica tube in a glove-box. The tube was set in a furnace and evacuated, then heated. The sample position was maintained until the solid precursor had melted and completely evaporated. The tube was then cooled to room temperature and transferred to the glove box where the tiles were removed and stored under an N_2 atmosphere prior to analysis.

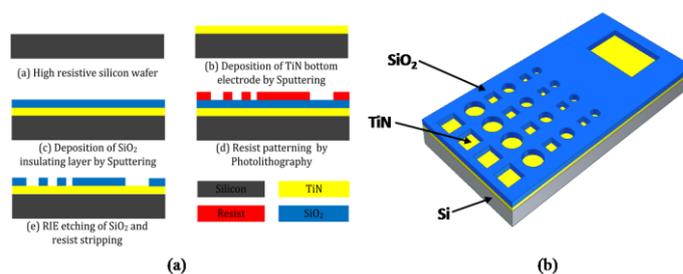


Fig. 1 Fabrication process of patterned substrate (a) and illustration of photolithographically patterned SiO_2/TiN substrate (b).

Electrodeposition: The electrolytes were prepared from $[\text{NBu}^n_4][\text{XCl}_4]$ or $[\text{NBu}^n_4][\text{YCl}_6]$, where $X = \text{Sb}, \text{Bi}$ and $Y = \text{Se}, \text{Te}$. The individual elements $\text{Sb}, \text{Bi}, \text{Se}, \text{Te}$ and Sb_2Te_3 were deposited potentiostatically onto TiN film electrodes. All depositions were undertaken in CH_2Cl_2 solution in a glove box.

3. RESULTS AND DISCUSSION

A. Thin film Deposition by LPCVD

The film morphology was analyzed by SEM. SnSe_2 is deposited as hexagonal plate crystallites lying perpendicular to the substrate. XRD measurements confirmed the deposition to be crystalline hexagonal SnSe_2 with no evidence of presence of other phase. The thicknesses of the films can be tuned by the amount of precursor as shown in where the crystallites lying flat on the surface form a thinner film with thickness around a few hundred nanometers.

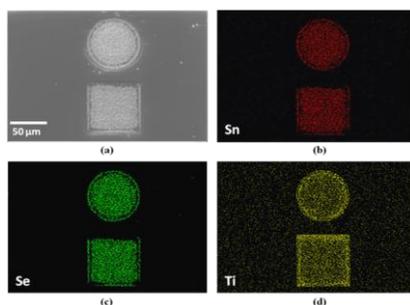


Fig.2: SEM image (a) and EDX element maps (b) – (d) confirming the selective deposition of SnSe_2 occurring only within the holes (80 μm diameter) with growth occurring preferentially onto the TiN surface.

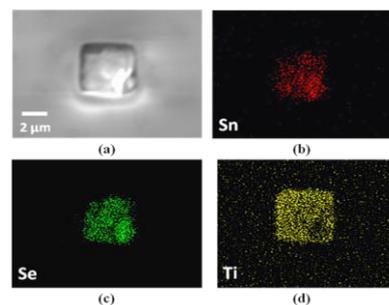


Fig.3: SEM image (a) and EDX element maps (b) – (d) confirming the selective deposition of SnSe_2 occurring only within the 5 μm size hole onto the exposed TiN surfaces.

LPCVD of SnSe_2 using patterned substrates resulted in remarkably high selectivity for film growth onto the exposed (conducting) TiN regions within the holes, but not onto the SiO_2 . This was observed both for the large (80 – 100 μm diameter) and also for the smaller (5 μm diameter) holes, as illustrated in Fig.2-3.

An even better selectivity was observed for Bi_2Te_3 deposited on the patterned substrate as shown in Fig.4. It is clear that the selectivity has the potential to go down to the nanometer regime Fig. 4(b).

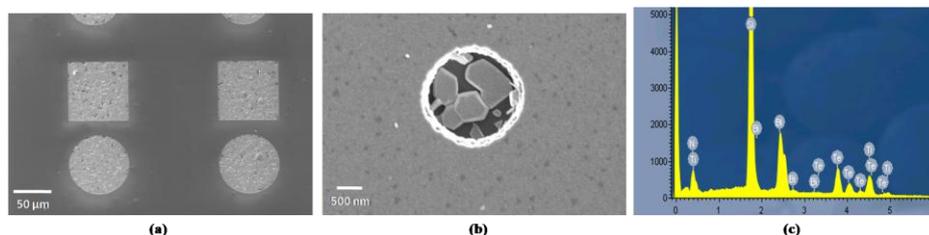


Fig. 4: SEM images showing the selective deposition of Bi_2Te_3 occurring only within the holes with diameter of 80 μm (a) and 1 μm (b) and EDX (c).

B. Thin Film Deposition by Electrodeposition

The electrodeposition of elemental films of bismuth, antimony, selenium and tellurium prepared on TiN cathodes resulted in thick films of the crystalline elements from a room-temperature non-aqueous electrochemical system. The elements show different morphologies, originating from their crystal structure and the electrodeposition conditions. All elements were detected in significant quantities and with high purity.

The deposition of binary phase change Sb_2Te_3 was achieved by combining the Sb and Te containing electrolytes and optimization of the deposition conditions. Fig.5 shows an initial deposition of Sb_2Te_3 into the patterned substrates. The as-deposited Sb_2Te_3 was found to be amorphous. It is clear that deposition is selective to the TiN holes and also occurs easily in the smallest (1 μm diameter) holes. This provides a very promising future for depositing into holes with diameters in the nanometer scale. Switching from amorphous to crystalline phases was achieved by annealing the film above its crystallization temperature in oxygen-free conditions, as shown in Fig.6.

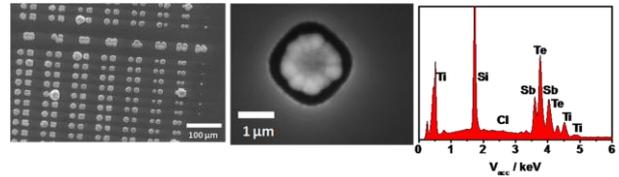


Fig.5: SEM and EDX images of Sb_2Te_3 deposited by electrodeposition.

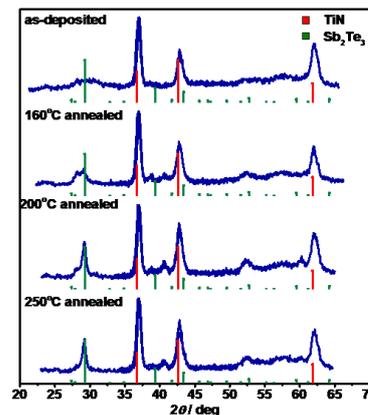


Fig.6: XRD spectra of Sb_2Te_3 films annealed at different temperatures.

4. CONCLUSION

We present here two technologies for selective deposition of phase change materials. Phase change SnSe_2 and Bi_2Te_3 have been deposited onto lithographically patterned SiO_2/TiN substrates by LPCVD showing strongly preferred deposition onto conducting TiN surfaces. A simple electrolyte system suitable for the electrodeposition of a range of elements from non-aqueous solvents has been established. The capability for depositing the binary phase change material Sb_2Te_3 has been demonstrated using this system. This ability opens the possibility to prepare more binary and ternary phase change materials. The electrochemical system is well suited to the preparation of these materials onto complex nanostructured substrates, providing an advantage over conventional techniques.

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Biographies

Ruomeng Huang received his B.S. degree in Physics from East China Normal University, China in 2008 and his M.Sc. from the School of Electronics and Computer Science at the University of Southampton with Distinction in Nanoelectronics and Nanotechnology in 2010. He is currently a PhD research student within the Nano group in the School of Electronics and Computer Science at the University of Southampton under an EPSRC funding. His research involves in development and characterization of novel deposition methods for phase change materials.