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Hot-Wire Chemical Vapor Deposition of Chalcogenide Materials for Phase Change Memory Applications

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Chalcogenide-based phase change memories (PCM) constitute the most promising candidate to scale nonvolatile-memory technology beyond the Flash memory architecture.[1,2] One of the technological issues that determines the integration of these new materials is the deposition method. Demonstrator chips based on chalcogenide PCMs, mainly $Ge_2Sb_2Te_5$, grown by sputtering techniques have already been fabricated.[3] Recently, the delivery of the first phase change memory prototype was announced.[4] However, because of the continued down-scaling of nanoelectronic device architectures, greater control of film deposition over nonplanar structures than so far achieved by sputtering is required.[5] This would allow lower programming currents, which lead to improved performance and lower costs. Metal organic chemical vapor deposition (MOCVD) is a very attractive method for growing layers because it enables the production of thin films with better conformality and composition control, including doping possibilities, and increased manufacturing throughput compared to sputtering techniques.

Recently, some attempts to apply MOCVD[6–9] or similar ALD[9,10] (atomic layer deposition) techniques for depositing ternary Ge−Sb−Te (GST) materials have been made. In these works, the application of plasma power and H_2 as reactant gas for process activation was essential in obtaining nearly stoichiometric $Ge_2Sb_2Te_5$ films. However, the precise control of composition, surface smoothness, and film thickness is still rather difficult for GST due to the narrow window of precursors' compatibility and deposition conditions. Simple thermal MOCVD without additional process activation usually results in rough films with incomplete lateral growth, even if the composition of the deposit is close to stoichiometric $Ge_2Sb_2Te_5$.[6]

In this communication, we report on the successful growth of chalcogenide films with required functional properties for PCM applications by the combination of hot-wire MOCVD (HW-CVD) and pulsed liquid injection (l.i.) MOCVD.[11] The elaborated method (HW-l.i.-CVD) is easily integrable because it does not require the use of plasma and/or hydrogen. The inherent key advantages of this deposition technique are the greater control of film composition, including doping possibility, and conformality over nonplanar structures, superior to those obtained by sputtering. Moreover, because of the catalytic decomposition of precursors and the use of diluted solutions, improved surface quality, higher growth rates, and wider precursor compatibility than with conventional thermal MOCVD are reached.

HW-CVD is largely used for device-quality silicon-related applications, mainly photovoltaic, at the research and industrial levels.[12] However, it has never been used for the growth of GST materials. In this technique, source gases are catalytically decomposed under a vacuum on a hot wire (tungsten filament at about 1800 °C) placed at some distance before the substrate. In our case, the thermal stability of Ge, Sb, and Te metal-organic (MO) precursors is usually lower than that of Si MO precursors, while the Ge, Sb and Te radicals formed during precursors decomposition may evacuate from the hot wire more easily than Si. Thus, for GST film deposition, very high wire temperature is not necessary, which simplifies the application of HW-CVD for chalcogenide materials.

In this study, $Ge(NMe_2)_4$, $Sb(NMe_2)_3$, and $Te(i\text{-}Pr)_2$ precursors were used for GST depositions. However, various other Ge, Sb, and Te precursors might be used as well. These sources were chosen due to their compatibility in a normal CVD process where the deposition is controlled by the substrate temperature. The described hot-wire technique

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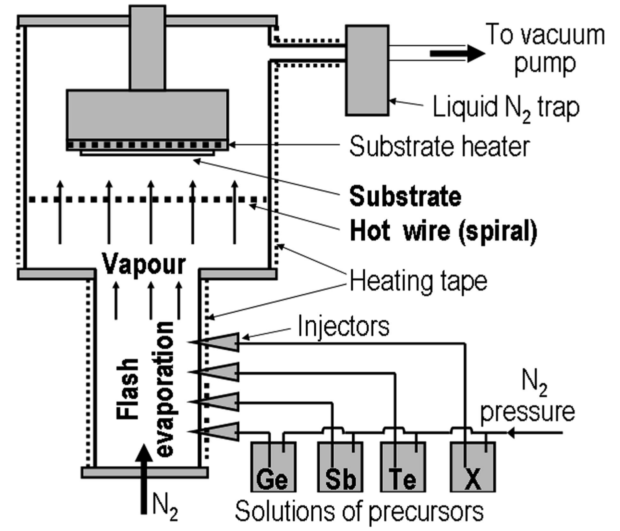

Figure 1. Simplified scheme of combined hot-wire CVD−pulsed liquid injection system for deposition of GST materials.

thermally activates these materials in a manner that negates their individual decomposition characteristics and in the future it may be possible to employ alternative Ge, Sb, Te precursors in combinations not possible in standard CVD approaches. The sources can be introduced into the reactor as vapors by passing a carrier gas through bubblers containing liquid precursors; however, to simplify the precursor dosimetry and for better composition and thickness control, we combined HW-CVD with principles of pulsed liquid injection CVD. In this case, diluted precursors solutions (0.05−0.2 M) in toluene were used. The use of diluted solutions instead of pure precursors as well as a high yield of precursor decomposition induced by hot wire allow a reduction of precursor consumption.

Before starting with HW-l.i.-CVD process we had investigated depositions by simple thermal CVD using the same precursors and while amorphous or well crystallized Sb_2Te_3, GeTe, and $GeSb_2Te_4$, $Ge_2Sb_2Te_5$ phases were deposited in the 270−400 °C temperature range, the layers were not fully continuous, rough, and powderlike.

A simplified scheme of the cold walls research HW-CVD system is given in Figure 1. The microdoses (several microliters) of precursor solutions are injected by pulses into a hot evaporator using computer-controlled electromagnetic injectors. After flash evaporation of injected microdoses under a vacuum, the resulting vapor mixture is transported by nitrogen gas into a deposition chamber. Prior to reaching the substrate, the vapors pass through a hot-wire spiral installed in front of the substrate holder. A Thermocoax heating element (1 mm in diameter and 1.5 m length) constituted the hot wire. Precursor decomposition on the hot wire and simultaneous evacuation at low pressure of residual Ge, Sb, Te radicals from wire yields specular film on the cooler substrate. Film composition is controlled by the length and frequency of pulses, whereas the thickness is directly related to the number of pulses. To avoid the condensation of precursor vapors, the quartz walls of the deposition chamber as well as the walls of the evaporator and vacuum lines are heated (~100−180 °C) by heating tapes. Film phase composition was studied by X-ray diffraction (XRD, Cu Kα radiation), morphology, and elemental composition by scanning electron microscope (SEM) equipped with energy-dispersive spectroscopy (EDS). Surface roughness was studied by atomic force microscopy (AFM), and film thickness was measured by X-ray reflectivity and profilometry.

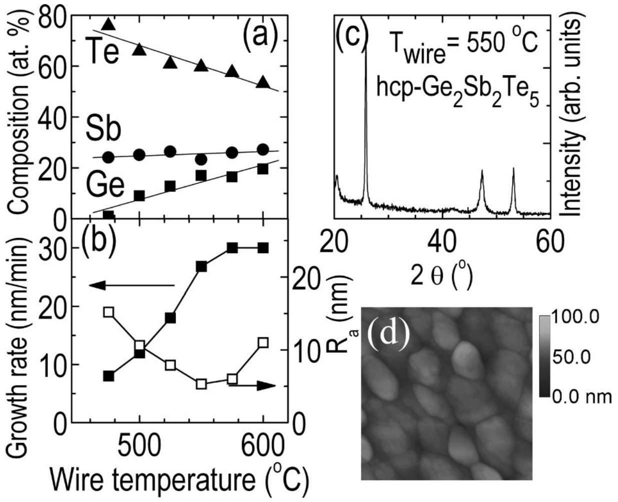

Figure 2. (a) Composition and (b) growth rate and roughness average R_a of ternary Ge−Sb−Te films in relation to hot wire temperature (film thickness increases from 20 to 75 nm); (c) XRD pattern of film grown on Si/SiO_2 substrate at wire temperature 550 °C; and (d) AFM image (2 × 2 μm scan) of film grown at wire temperature 575 °C. Composition in (a) is an average result of five analyses in different laterally dispersed points on a 4 cm^2 surface (lateral dispersion of the results is within 5−10%).

The influence of the total pressure is highly relevant for the deposition process. When the pressure is too high, the efficiency of precursor decomposition and radical evacuation from the wire is reduced and the deposited film is partially formed by decomposition of precursors directly on the substrate surface. This leads to rougher films rather similar to those obtained by simple thermal CVD. Pure rapid HW-l.i.-CVD growth was observed at about ≤20 Torr pressure.

To test the influence of the hot wire temperature, we performed a series of depositions using different wire temperatures with all other parameters unchanged. The distance between wire and substrate was fixed at 3 cm, substrate temperature 300 °C, nitrogen flow rate 50 sccm, pressure ~1 Torr. Precursor solutions were injected in a fixed-volume ratio into evaporator (150 °C) with a gap of 20 ms between the pulses of different precursors in cycle, and 1 s interval between injection cycles (in total 150 cycles or about 2.5 min for deposition). The change in composition, growth rate, and roughness of ternary Ge−Sb−Te films in relation with hot wire temperature is presented in Figure 2. The increase in wire temperature results in the increase of Ge and decrease of Te content, while Sb content in films remains almost constant, Figure 2a. The surface roughness average R_a of deposited films reaches the minimum (~5−6 nm) at T_{wire} = 550−575 °C, Figure 2b. The film growth rate reaches full saturation at T_{wire} = 575 °C indicating a maximum efficiency of precursor decomposition and radical evacuation processes on the hot wire. Starting from a wire temperature of 525 °C, films become well-crystallized, rather smooth, continuous, hard, and well-adhered to Si, Si/SiO_2, and glass substrates. The hcp-$Ge_2Sb_2Te_5$ phase was found

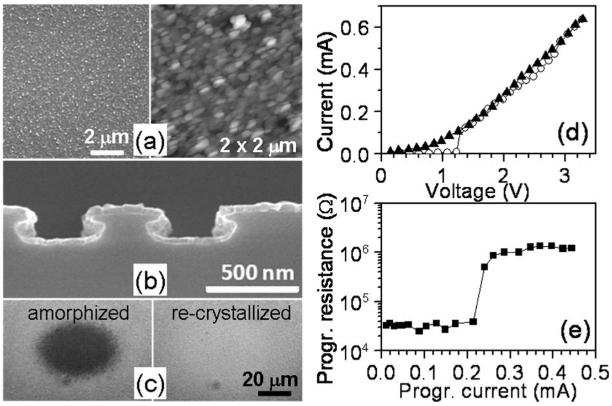

Figure 3. (a) SEM (left) and AFM (right) images of 50 nm thick $Ge_2Sb_2Te_5$ film on Si/SiO_2 substrate grown under optimized conditions (550 °C/300 °C, 5 cm distance, 10 Torr, 2000 sccm N_2); (b) SEM cross-section showing the isolation trenches in the PCM devices with GST film; (c) phase switching of a 45 nm thick GST film obtained upon laser pulse irradiation (8 ns, 800 nm) between amorphous (low-reflectivity) and crystalline (high-reflectivity) states (optical contrast ∼25%), all on the same surface region; (d) current−voltage ($I-V$) characteristic of a PCM cell for both the set (black triangles) and reset (white circles) state; (e) programmed resistance vs programming current ($R-I$ curve) for PCM cell originally programmed in the conductive state.

dominant in films grown at $T_{\mathrm{wire}} \geq 550$ °C, Figure 2c. Films grown at low wire temperature are rough and contain smaller crystallites (not shown), whereas those grown at higher wire temperature (≥525 °C) contain bigger (several hundreds of nanometers, Figure 2d) crystallites.

Additional optimization of deposition conditions was made in order to decrease the crystallites size and surface roughness of GST films. Smaller crystallites and smoother $Ge_2Sb_2Te_5$ films (R_a about 3−4 nm) were obtained (as shown in Figure 3a) at higher distance between the hot wire and substrate and by adjusting the structure of precursor injection cycle, the pressure, and gas flow rate. Wire and substrate temperatures were 550 and 300 °C, respectively. Under optimized conditions, well-crystallized, continuous, and smooth GeTe and Sb_2Te_3 films were obtained as well.

Results of the functional characterizations of the grown films are presented in Figure 3. A SEM cross-section image of μ-trench structure in Figure 3b shows the good conformality of the GST layer grown by HW-(l.i.)-CVD. Figure 3c shows laser pulse-induced switching between different material phases, i.e., crystallized (high reflectivity) and amorphous (low reflectivity), as obtained in a 45 nm GST film grown on Si/SiO_2, similarly to results obtained for sputter-deposited GST films.[13] We observe a comparable behavior (in terms of laser pulse fluences, pulse duration, and number of pulses required for recrystallization and amorphization) in both sputter-deposited and HW-l.i.-CVD films of the same thickness.

A 40 nm thick layer of GST film was used for fabricating PCM cells based on the μTrench architecture.[14] Panels d and e in Figure 3 report the current−voltage ($I-V$) characteristics and the programming curve ($R-I$), respectively. As shown in Figure 3e, when the programming current reaches 200 μA, the cell resistance starts to increase, and a resistance change between "set" and "reset" states of about 2 orders of magnitude can be achieved with a programming current of about 400 μA, similarly to PVD grown GST films.[14] The corresponding programming voltage drop is around 2.5V, but it is mainly due to the large access resistance available in these test devices (about 2.5 kΩ). The phase change transition has been demonstrated to be reversible and hundreds of cycles with full electrical functionality have been observed.

In summary, we demonstrated the feasibility of high rate deposition of controlled layers of chalcogenide materials for PCM applications using HW-liquid injection-CVD. HW-l.i.-CVD is capable of producing chalcogenide films without the use of plasma and/or hydrogen, and with clearly better quality than simple thermal CVD. Preliminary electrical results show promising characteristics with reproducible phase-change behavior. The optical phase switching between amorphous and crystalline states has also been demonstrated in these films with functional characteristics for applications in memory devices. Therefore, HW-l.i.-CVD GST emerges as an appealing technology that can enable the development of high-aspect-ratio PCM cells with improved programming characteristics.

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