Hot-wire chemical vapor growth and characterization of crystalline GeTe films


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Films of germanium telluride (GeTe) were grown by chemical vapor deposition (CVD) using pulsed liquid injection/flash evaporation principle to introduce the metalorganic precursor vapors. Simple thermal CVD with no additional process activation and CVD employing hot-wire remote catalytic activation of the precursor decomposition process were investigated and compared. Ge(NMe2)4 and Te(iPr)2 precursors in the form of diluted solutions in toluene were used as source materials for the depositions. Film composition was controlled changing the ratio of injected precursors, while the thickness was directly related to the number of injection pulses. Growth of GeTe films with a clearly better quality was demonstrated via the hot-wire-activated CVD process when compared to the standard thermal CVD. The influence of substrate temperature and deposition pressure on film crystallinity and morphology was studied. Reversible optical phase switching was demonstrated in 40–50 nm thick GeTe films on Si/SiO2 substrates.

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1. Introduction

Ge–Te, Sb–Te and Ge–Sb–Te alloys are under wide investigation for applications in the field of optical and electrical storage due to their fast reversible crystalline-to-amorphous phase transition induced by either laser or electrical pulses. Phase-change materials are now successfully employed in the optical data storage and are becoming promising candidates for the future electronic storage applications [1]. Chalcogenide-based phase-change random access memories (PC-RAM) constitute the most promising candidate to scale non-volatile-memory technology beyond the flash memory architecture [2]. Among pseudobinary GeTe–Sb2Te3 materials in the Ge–Sb–Te system, Ge2Sb2Te5 (GST) is the best-known candidate and has been most widely studied for PCM. Demonstration chips based on GST, grown by sputtering techniques, have already been fabricated [3]. However, both binary constituents, i.e., GeTe and Sb2Te3, can also be used for the phase-change recording. So they have also been investigated for such applications in thin film [4–8] or nanowires [9–11] form.

One of the technological issues that determine the integration potential of these new materials is the deposition method. Due to the continued down-scaling of nanoelectronic device architectures, greater control of film deposition over non-planar structures, than so far achieved by sputtering, is required [12]. Metalorganic chemical vapor deposition (MOCVD) is an attractive method to address the targeted device structures because it is capable of providing better conformity and composition control, and increased manufacturing throughout compared to the direct physical vapor deposition techniques.

Some attempts to employ MOCVD [13–16] or similar atomic layer deposition (ALD) [16,17] techniques for depositing ternary Ge–Sb–Te materials have been made. In these works, the application of plasma power and/or H2 as reactant gas for process activation was essential to obtain nearly stoichiometric GST films with rather high growth rate. Simple thermal MOCVD without process activation usually results in rough films with incomplete lateral growth, even if the composition of the deposit is close to stoichiometric GST [13]. Only a limited number of works may be found on MOCVD growth of GeTe films [7,18]. Authors of the first work [7] used Ge(allyl)4 and Te(iPr)2 precursors. However, they state that Ge cannot be introduced into film without the presence of vapors of Sb precursor (Sb(iPr)3) in the reaction zone. Moreover,
they found that a simultaneous introduction of Ge, Te and Sb precursors into reactor produces only Sb$_2$Te$_3$ films. So a two-step process was essential to produce GeTe films. In the first step, a Ge film was grown from Ge (allyl)$_4$ in the presence of Sb(iPr)$_3$ in vapor phase, after this Te deposition was performed on the grown Ge film and GeTe films formed due to reaction between Ge and Te during this step. In Ref. [18], only very rough films containing big grains on smoother matrix were obtained using H$_3$Ge(iBu) and Te(iPr)$_2$ as precursors.

Recently, we reported the first results obtained from the application of a hot-wire CVD (HW-CVD) (or catalytic-CVD) technique for the growth of smooth GST films exhibiting reversible electrically and optically induced phase-change switching [19]. In this paper, we present a detailed study on the growth of germanium telluride (GeTe) films by HW-CVD (in combination with pulsed liquid injection MOCVD [20]), in comparison with results we obtained on GeTe growth by standard thermal MOCVD. HW-CVD is largely used for device quality silicon-related applications, mainly photovoltaic, at research and industrial level [21]. In this technique, source gases are catalytically decomposed on a hot-wire placed at some distance before the substrate to allow film deposition from highly active species. In order to obtain full decomposition of the metalorganic precursors and evacuation of the radicals formed from the hot-wire towards the substrate typically high temperatures (1700–1800 °C) are needed. However, the thermal stability of the Ge and Te MO precursors used in this study is lower than that of Si precursors, and moreover, the Ge and Te radicals formed during precursors decomposition may evacuate from a hot-wire more easily. Thus, in the case of GeTe film deposition, reduced wire temperatures can be utilised.

2. Experimental details

In our work, Ge(NMe$_2$)$_2$ and Te(iPr)$_2$ precursors were used for GeTe deposition. The sources can be introduced into the reactor as vapors by passing a carrier gas through bubblers containing liquid precursors. However, in order to simplify the precursor dosimetry and for better composition and thickness control, CVD and HW-CVD were combined with the principles of pulsed liquid injection CVD [20]. In this case, diluted precursor solutions (0.2M in toluene) were used. These precursors solutions were kept in special stainless-steel tanks (bubblers), each connected to a separate injector. Films were grown on Si/SiO$_2$ substrates.

A simplified schematic of the vertical cold-wall CVD system used for the depositions has been given in Ref. [19]. The substrate was heated by an internal resistive heater installed inside the stainless-steel substrate holder. The same reactor was used for both versions of CVD depositions, but in the case of HW-CVD, a hot-wire was installed at some distance from the substrate holder. A Thermocoax heating element in Inconel sheet (1 mm in diameter and ~1.5 m length) turned into a spiral constituted the hot-wire. In order 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 were heated (100–150 °C) by heating tapes.

The micro-doses (several μL) of each precursor solution were injected as pulses into a hot evaporator using two separate computer-controlled electromagnetic injectors. There are many possibilities to change the injection cycle structure by changing injector opening times and the frequencies as well as the sequence of pulses of different precursors. After flash evaporation of the injected micro-doses under vacuum, the resulting vapor mixture was transported by nitrogen gas into a deposition chamber. In the standard CVD configuration precursor vapors thermally decompose directly on a hot substrate forming a coating. In HW-CVD, prior to reaching the substrate, the vapors pass through a hot-wire spiral. Catalytical precursor decomposition on the hot-wire and simultaneous evacuation at low pressure of residual Ge and Te radicals from wire yield growing specular GeTe film on the cooler substrate. Film composition is controlled by the length and frequency of injection pulses of different injectors whilst the thickness is directly related to the number of pulses.

In addition to a cold-wall reactor, a hot-wall reactor configuration was also tested for the thermal CVD of GeTe films. In the hot-wall version, the above reactor design was used except for the substrate heating which was achieved via the hot quartz walls using an external resistive furnace.

Films phase composition was studied by X-ray diffraction (XRD, Cu-K$_\alpha$ radiation), morphology and elemental composition by scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). Surface roughness was studied by atomic force microscopy (AFM) and film thickness was measured by profilometry. Pulsed laser irradiations were performed using a Q-switched Ti:sapphire laser operating at 800 nm wavelength with a pulse duration of 8 ns. The laser beam was focused onto the sample surface to an elliptical spot size of 100 x 59 μm$^2$ (1/e$^2$ intensity diameters) and its intensity distribution was determined to be Gaussian [22]. The photoduced phase changes were observed and recorded in situ with an optical microscope composed of light-emitting diode (illumination source), imaging optics (long working distance microscope objective and a tube lens) and a 12 bit CCD camera.

3. Results and discussion

3.1. Simple thermal CVD growth of GeTe layers

Film growth by simple thermal CVD was studied using both cold-wall and hot-wall CVD reactor designs. Various deposition conditions were tested: substrate temperature (300–450 °C), evaporator temperature (100–200 °C), nitrogen flow rate (50–6000 ccm), injection parameters and injection cycle structure. Fig. 1(a) and (b) shows XRD patterns and SEM images of GeTe films grown at different substrate temperature in the hot-wall reactor version, pressure 100 Torr, nitrogen flow 100 ccm, evaporator temperature 100 °C. Ge and Te precursors solutions were injected into the evaporator almost simultaneously, with a gap of 20 ms. Ge–Te injection frequency was 2 Hz, total number of injection cycles was 300. Films grown at 300 °C were almost amorphous. Increasing the deposition temperature increases the crystallization degree of the rhombohedral GeTe phase. XRD patterns of films grown at high temperature shows high texture degree of GeTe crystallites. Film morphology also changes with deposition temperature. At low temperature, films contain smaller and denser crystallites, while an elevated temperature results in bigger more separated crystallites.

No clear difference in layers quality was found between hot-wall and cold-wall CVD reactors. The GeTe layers grown in both reactor versions were not fully continuous, rough and soft (scratch test showed poor adhesion to the substrate).

3.2. HW-CVD growth of GeTe layers

In the HW-CVD study of GeTe growth, two series of depositions were performed in order to investigate the influence of deposition pressure and substrate temperature. Hot-wire distance from substrate, wire temperature, evaporator temperature and nitrogen
flow were set at 5 cm, 550 °C, 150 °C and 2000 ccm, respectively, at the same values optimized previously for HW-CVD deposition of GST films [19]. Solutions of Ge and Te precursors were injected by separate injectors into the evaporator, in a fixed volume ratio.

The series of depositions at different pressure was made at a substrate temperature of 290–295 °C. The injection cycle structure was Ge–Ge–Te–Ge–Ge with gaps of 30 ms between pulses, and a gap of 3 s between cycles (in total 100–120 cycles, or about 5 min for deposition). It was found that Ge incorporation into a deposited film is more difficult than Te, so the Ge precursor has to be injected in excess. Fig. 2 shows the changes of the growth rate, surface roughness and composition of GeTe films in relation to the deposition pressure. Film thickness in this series varied from 35 to 105 nm. The growth rate shows little dependency on pressure in the range from 1 to 15–20 Torr but increases more significantly with higher pressure (Fig. 2(a)). Rather similar changes were observed in the plot of average surface roughness (Ra) vs. deposition pressure (Fig. 2(b)), i.e., films become clearly rougher when grown at higher pressure. Film composition was found to be almost independent of system pressure (Fig. 2(c)) with the Te/Ge ratio in films dispersed around the average value 1.25. Deviation of the analysis results from stoichiometric 1:1 Te/Ge may be partly related to the low precision of EDS analysis for very thin films due to an absence of thin film standards.

Fig. 3(a) and (b) show XRD patterns and AFM scans of GeTe films grown at 290–295 °C and a range of pressures. Well-crystallized films of rhombohedral GeTe (pdf-47–1079) may be deposited at all of the studied pressures. Lower pressure (~1–20 Torr) results in well-textured GeTe films, whilst at higher pressures the GeTe (2 0 2) reflection clearly observed in the XRD data shows a larger disorientation of crystallites. AFM scans of GeTe films are in agreement with XRD patterns, i.e. textured crystallites are visible in films grown at low pressure and rough films with more crystallite disorientation seen at higher pressure. Small gaps between crystallites were observed in the AFM scan of the film grown at the lowest pressure (~1 Torr). Such morphology resulted in a higher Ra value and higher resistance of this film compared to other films grown at low pressure. It seems that very low pressure is not favourable for the growth of dense GeTe film at high temperature, probably due to too low concentration of precursors vapors in the reactor and their high velocities resulting in low residence times.

These studies show that the total pressure is highly relevant for the HW-CVD process. The growth of GeTe films in the lower pressure range (about ≤20 Torr) may be considered as pure HW-CVD and gives the best films. When the pressure is increased,
the efficiency of precursor decomposition and radical evacuation from the hot-wire is reduced and the deposited film is partially formed by decomposition of precursors directly on the substrate surface. In the pressure range above 20 Torr the increase of contribution of simple thermal CVD into the film growth process is shown to lead to rougher, poorer quality films rather similar to those obtained by simple thermal CVD.

The influence of substrate temperature was tested under similar conditions. Deposition pressure was set at 15 Torr and a series of films was grown at different substrate temperatures. It should be noted that the hot-wire heats the substrate holder and the substrate during the deposition, so the film growth occurs in a range of increasing temperature. The degree of temperature rise is larger at lower starting substrate temperatures. In all figures a temperature range or the substrate temperature at which we start precursor injection into reactor (growth start temperature) is indicated. The films from the previous studies on pressure dependence contained some excess Te according to EDS, so in this temperature series an increase of Ge content was attempted by including two additional Ge pulses into the injection cycle (Ge–Ge–Te–Ge–Ge, in total 50–70 cycles).

Fig. 4 shows the changes of the growth rate, surface roughness and composition of GeTe films in relation to deposition temperature. Film thickness in this series varied from 40 to 55 nm. The growth rate shows little dependency on deposition temperature, although some growth rate decrease may be observed in the intermediate temperature range (Fig. 4(a)). The smoothest films (Ra~2.5 nm) were grown at starting temperature 210 and 230 °C (Fig. 4(b)). Despite the increase of Ge content in the injection cycle, all films still contained Te excess independently of deposition temperature (Fig. 4(c)). Te/Ge ratio in films of this series was dispersed around the average value of 1.2, the value slightly lower than for films of the pressure series (Te/Ge=1.25).

Fig. 5(a) and (b) shows XRD patterns and AFM scans of GeTe films grown at 15 Torr pressure and at different temperatures. Decreasing the temperature results in the decrease of crystallization and texturation degree of GeTe films. Only films grown at a high start temperature (280 and 290 °C) are...
well-crystallized and textured. Films grown at the lowest studied temperature do not show any texture and are poorly crystallized.

AFM scans in Fig. 5(b) correlate well with XRD data. Film grown at the highest studied temperature contains rather big flat textured crystallites. The next film contains similar morphology, but the crystallites are smaller and the surface roughness is somewhat lower. The films grown at intermediate temperatures are composed of very small dense crystallites resulting in smooth surfaces. The poorly crystallized film grown at the lowest temperature is much rougher, formed from bigger and less dense grains.

In an attempt to increase the degree of crystallization of films deposited at low temperature they were annealed for 30 min at 350°C under nitrogen (~1 atm). However, no improvement in crystallization was observed, moreover, a weak additional Te peak appeared in XRD patterns of annealed films showing partial tellurium segregation during the annealing (Fig. 6(a)). In contrast, no Te segregation has been observed by XRD during the similar annealing of well-crystallized samples grown at higher temperature (Fig. 6(b)).

3.3. Functional characterization of HW-CVD grown GeTe layers

We have performed optical characterization of the phase switching properties in GeTe thin films grown by HW-CVD using ns laser pulses. The phase switching was accompanied with pronounced changes of the optical reflectivity, corresponding to either low-reflectivity amorphous phase, i.e. Fig. 7(a) and (c), or high-reflectivity crystalline phase, i.e., Fig. 7(b) and (d). In Fig. 7(a), the amorphization was induced in an as-grown crystalline film upon single intense pulse irradiation at constant fluence of 116 mJ/cm². Subsequent re-crystallization using single laser pulse was not possible, which may be attributed to the shorter pulse duration used in this study (8 ns) as compared to the minimum pulse duration required for single-pulse crystallization of amorphous GeTe, i.e. 30 ns [23]. Therefore, multiple laser pulses at constant fluence of 42 mJ/cm² were used in order to re-crystallize the amorphous spots in Fig. 7(b) and (d). Further irradiations of these re-crystallized regions, aimed at inducing re-amorphization (Fig. 7(c)) were performed at laser fluences slightly lower than 42 mJ/cm².
lower than the fluence chosen to induce the first amorphization. Since the actual phase of the as-grown crystalline GeTe and the laser-induced re-crystallized phase, i.e., Fig. 7(b), may slightly differ in terms of film surface morphology, the laser fluence used for re-amorphization in Fig. 7(c) was lower, i.e. 108 mJ/cm². The re-amorphized regions showed a similar optical contrast as the amorphous spot induced on the as-grown sample (Fig. 7(a)). Most probably due to lower laser fluence used in the first cycle, the lateral reflectivity profiles (across the spot centers) were extracted from images (a)–(d) and normalized to the reflectivity level of the as-grown film. During the second cycle both re-amorphization (curve 3) and re-crystallization (curve 4) reflectivity profiles remained essentially unchanged and the reflectivity values were consistent with those observed during the first cycle. Yet, the lateral extension of the re-amorphized spot (Fig. 7(c)) is smaller than that of the amorphous spot induced on the as-grown sample (Fig. 7(a)), most probably due to lower laser fluence used in the former case.

4. Conclusions

Two CVD versions—standard thermal CVD and hot-wire activated CVD were studied and compared for the growth of GeTe layers for phase-change memory applications. Both CVD versions were combined with a pulsed liquid injection/flash evaporation principle for precursor delivery. Ge(NMe₂)₄ and Te(iPr)₂ diluted solutions (0.2 M) in toluene were used as the precursor materials. HW-CVD is demonstrated to be capable of producing GeTe films of clearly better quality than simple thermal CVD. The influence of deposition pressure and temperature to films growth rate, composition, morphology and crystallinity was studied. These two parameters mainly determine GeTe film crystallinity, texture, crystallite size and surface roughness. Optical phase switching between amorphous and crystallized states have been demonstrated using ns laser pulses in GeTe films grown by HW-CVD. Although preliminary, these results show very promising functional properties of these films allowing for reproducible phase cycling with a limited number of cycles. Although gradual surface degradation after repeated laser-induced amorphization–crystallization processes was observed, further optimization of the film deposition procedure should improve the required GeTe films quality so as to allow for a higher number of phase cycles.

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