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Thermally induced irreversibility in the conductivity of germanium nitride and oxynitride films

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ABSTRACT

We report the evidence for irreversible changes in the conductivity, $\sigma(T)$, of a-Ge_3N_x ($3.7 < x < 4.6$) and quasi-stoichiometric a-$Ge_2O_yN_x$ thin films occurring at $T \gtrsim 630$ K, under high vacuum conditions. We have found that $\sigma(T)$ curves not only depend on the material properties but also on the thermal history undertaken by films. The irreversibility in $\sigma(T)$, during heating in vacuum, is correlated to the transformation of the native GeO_2 into volatile GeO. Thermal annealing in N_2 atmosphere, on the contrary, results to extend film stability up to 973 K. At higher *T*, domes and pits are formed onto the film surface, due to the strong effusion of N-rich volatile species. Unstable N-Ge bonds can explain both the nitrogen thermodynamic instability and the Ge nano-crystallisation process occurring in a-Ge_3N_x films, upon heating until 1023 K. Compared to a-Ge_3N_x, quasi-stoichiometric a-$Ge_2O_yN_x$ is both more insulating and more stable upon heating up to 1023 K under N_2 flow, that makes it a suitable passivating layer material for the fabrication of electronic devices.

1. Introduction

Germanium based nitrides and oxynitrides, both in crystalline and amorphous phases, are dielectric materials interesting for several technological applications [1,2]. With respect to GeO_x native oxide, composed of the unstable GeO and hydrosoluble GeO_2 [3,4], GeN as well as GeON alloys can compete with the high stability, ease of formation and thickness control of SiO_2 for Si based devices [1]. Germanium nitride and/or oxynitride have been tested to be good candidates as dielectric layer for phase change memory [2,5] and as gate interlayer for capacitors and transistors fabrication as well [6]. Ge_3N_4, with a band gap of ≃4.5 eV, is a good candidate as a passivating layer for metal oxide semiconductor capacitors [7] and for the fabrication of high performance and low leakage current Ge *p-n* junctions as well [8]. This last kind of application has been pushing forward with research activity to develop high performance γ-ray detectors based on high purity Ge crystals (HPGe) [9].

Despite interesting potential applications, the electrical properties of GeN and GeON based dielectric alloys are only partially known since the huge insulating properties of this class of materials represents an obstacle to carry out reliable measurements.

Data reported in literature refer to under-stoichiometric a-GeN alloys, both H-free and hydrogenated, as well as nitrogen doped c-Ge and a-Ge [10]. For these systems, experiments have demonstrated that insulating properties of both Ge_3N_x and Si_3N_x deteriorate notably as the nitrogen concentration decreases far below $x \simeq 4$ [10].

In previous studies carried out on this class of materials, the authors investigated the properties of the as-deposited films and their electronic transport properties, aimed to find the optimal deposition parameters to fabricate thin layers having the best insulating properties. The effects of the deposition parameters on the electrical properties were also studied in a temperature range from R.T. up to 600 K [11,12].

We have extended the investigation to the thermal stability of a-Ge_3N_x and a-$Ge_2O_yN_x$ films upon high temperature annealing under a N_2 gas flow. Composition, structure, morphology and conductivity have been extensively studied in annealed samples. Compared to the other techniques used in this study, we have found that the electrical conductivity is very sensitive in detecting thermally-induced irreversible changes occurring during the measurements. The results obtained by the electrical characterisation of as-deposited films (Section 3.1) extend previous studies the reader is referred to [11,12].

2. Experimental

Thin films of a-Ge_3N_x and a-$Ge_2O_yN_x$ were deposited at room temperature (R.T.), by reactive r.f. magnetron sputtering. Deposition was

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Table 1
Properties of a-Ge_3N_x and a-$Ge_2O_yN_x$ films deposited under different conditions. From left to right: sample name; as-deposited film stoichiometry measured by the RBS technique (see the Section 2); bias (the average dc voltage acquired by the r.f. biasing of the sample, see the Section 2); gas mixture and relative flow; film thickness; Ge surface density; total deposition rate of the film; T_{max}: maximum annealing temperature under N_2 flow; film stoichiometry after annealing at 973 K. The target to substrate distance has been fixed at 5 cm for all samples, except for #*I* and #*L* fixed at 14 cm. The errors on the N and O values are around 5%.

Sample	Stoichiometry (as-deposited)	Bias (V)	Gas & Flow (sccm)	Thickness (nm)	n_{Ge} (at/cm^2)	V_{dep} (Ge$_{at}$/s cm^2)	T_{max} (K)	Stoichiometry (after TT)
#A	$GeGe_3N_{4.6}$	0	N_2, 40	124	4.3×10^{17}	1.0×10^{15}	923	$Ge_3N_{2.9}O_{1.3}$
#B	$GeGe_3N_{4.6}$	−20	N_2, 40	181	6.3×10^{17}	1.0×10^{15}	–	–
#C	$Ge_3N_{4.2}$	−40	N_2, 40	141	4.9×10^{17}	1.0×10^{15}	873	$Ge_3N_{3.5}O_{1.8}$
#D	$Ge_3N_{4.1}$	−60	N_2, 40	181	6.3×10^{17}	1.0×10^{15}	873	$Ge_3N_{3.7}O_{0.84}$
#E	$Ge_3N_{4.1}$	−80	N_2, 40	159	5.5×10^{17}	9.3×10^{14}	873	$Ge_3N_{3.3}O_{1.6}$
#F	$Ge_3N_{3.7}$	−100	N_2, 40	160	5.5×10^{17}	8.8×10^{14}	873	$Ge_3N_{2.8}O_{2.7}$
#G	$Ge_3N_{4.1}$	0	N_2 + Ar, 20 + 20	217	7.5×10^{17}	1.7×10^{15}	973	$Ge_3N_{4.3}O_{0.10}$
#H	$Ge_3N_{4.1}$	0	N_2 + Ar, 15 + 25	261	9.1×10^{17}	2.0×10^{15}	973	$Ge_3N_{4.2}$
#I	$Ge_2O_{1.2}N_{1.9}$	0	N_2 + Ar, 20 + 20	127	4.4×10^{17}	1.6×10^{14}	973	$Ge_2O_{1.3}N_{1.8}$
#L	$Ge_2O_{1.2}N_{1.9}$	0	N_2 + Ar, 20 + 20	43	1.5×10^{17}	1.6×10^{14}	973	–

carried out at 60 W, with a total gas flow of 40 sccm by using pure N_2 or Ar + N_2 gas mixtures (either at 20 + 20 sccm or 25 + 15 sccm of gas flows, respectively) in conjunction with a Ge target (99.999% of purity). The different substrates (silicon, carbon and sapphire) were placed on a sample holder at distances of 5 cm and 14 cm from the target. A set of samples (the so-called biased samples) was biased by a second RF source, which resulted in a mean dc voltage acquired by the layers ranging from 0 V to −100 V. In this way, a controlled ion-bombardment-assisted deposition, at a constant average ion energy, was achieved.

A mass spectrometer, Prisma Plus QMG 220 (Pfeiffer Vacuum), revealed water vapor as the main residual component in the deposition chamber. Parameters chosen for the deposition as well as the resulting film composition are reported in Table 1). A detailed investigation of the as-grown film properties has been reported elsewhere [11].

Investigation of different physical properties upon high temperature annealing required layer deposition on three different substrates, i.e. carbon, silicon and sapphire, during each run. As-deposited films were thermally annealed under N_2 flow (400 sccm) at 873 K, 923 K, 973 K and 1023 K for 1 h, by using a tubular furnace (Lindberg). Before sample annealing, several dry-cleaning vacuum cycles with pure N_2 gas (99.9999%) were done, in order to remove contaminants such as water vapour and CO_2. The heating and cooling ramps were fixed at 90 K/h.

Film stoichiometry was investigated at R.T. by Rutherford Backscattering Spectrometry (RBS), at the scattering angle of 160° on films deposited on carbon substrates by using a 2.0 MeV^{4}He$^+$ beam (Van de Graaf accelerator at the Laboratori Nazionali di Legnaro). Samples deposited on silicon substrates were characterised by means of glancing x-ray diffraction (XRD) using a Philips diffractometer equipped with glancing-incidence X-ray optics. The analyses were performed at 0.5° of incidence, using CuK$_\alpha$ Ni filtered radiation at 40 kV and 40 mA.

The vibrational dynamics of germanium nitride and oxynitride samples deposited on silicon substrates was probed by Fourier transformed infra-red (FT-IR) spectroscopy measurements. The transmittance spectra of the samples were recorded in the 4000–400 cm^{-1} range, using a spectrometer Jasco (model FTIR 660 Plus) with a resolution of 4 cm^{-1}. The surface morphology of the samples was investigated by a SEM (Tescan Vega3 XM) equipped with an energy dispersive spectrometry (EDS) detector.

For the characterisation of the electrical conductivity, $\sigma(T)$, films were deposited on sapphire substrates and the measure was carried out at dark in a small furnace operating in vacuum ($P < 10^{-5}$ mbar). Due to the extremely low conductance, *S*, exhibited by all films, a two co-planar contacts geometry was used, with Au pads sputtered onto the film surface near its borders. Film conductance was measured by electrometers (Keithley either mod. 617 or 6517B) operated in the V/I mode, i.e. applying a constant bias (typically 50 V) and measuring the current. Particular attention was paid to frequently check the insulation resistance of the whole measuring apparatus. In this respect, an improvement of the insulation resistance of the cables inside the furnace, occurred during the present study, allowed to extend the sensitivity of the measure of more than one order of magnitude. After this upgrade, the low limit of the system sets to $\approx 10^{-15}\ \Omega^{-1}$ from R.T. to about 600 K, attaining $\approx 10^{-12}\,\Omega^{-1}$ at 700 K. These values must be considered as the lowest detectable *S* in our films. As a consequence of this limit in the sensitivity of our apparatus, the real $\sigma(T)$ of several films saturates around R.T. (and in few films until ≈ 450 K) at $\approx 10^{-11}\,(\Omega\ \mathrm{cm})^{-1}$; at $\approx 10^{-9}\,(\Omega \mathrm{cm})^{-1}$ for the layers measured before the apparatus upgrade.

Thermal energy in the film was changed very slowly, with a rate of about 0.5 ÷ 1 K/min, in cycles from R.T. up to ≃600 ÷ 700 K and then back to R.T., without any break. Each *S*(*T*) curve was collected after *T* stabilisation to better than 1 K (typically 0.5 K). For every *T*, 25 ÷ 30 *S* (*T*) values were averaged to calculate the corresponding $\sigma(T)$ value.

It's worthwhile to note that, due to the particular conditions of measure established in this study, all investigated films have undergone a process equivalent to a thermal annealing in vacuum.

3. Results

3.1. Temperature stability of as-deposited films

We have systematically studied high *T* stability of a-Ge_3N_x and a-$Ge_2O_yN_x$ films measuring in vacuum their electrical behaviour as a function of temperature. Conductivity of as-deposited layers has been measured, during continuous thermal cycles both in the heating, $\sigma_H(T)$, and in the cooling, $\sigma_C(T)$ run. Due to the sensitivity limit of our measuring setup, conductivity has evidenced a saturation (except for #*F*) at $\approx 10^{-11}(\Omega\ \mathrm{cm})^{-1}$, below a *T* value ranging from 380 K to 460 K, ascribed to the insulation resistance of the apparatus (see the Section 2). For the first cycle, carried out from R.T. to 600 K, we have always found $\sigma_{H1}(T) \geq \sigma_{C1}(T)$[1] (Fig. 1) explained with the presence of a conducting layer onto the film surface. For some samples, we further checked that repeating the characterisation up to 600 K, the conductivity measured during the heating overlapped to that of the first cooling run[2] [12].

During the second cycle, carried out keeping the sample in vacuum and increasing the final *T* at 700 K, we have observed $\sigma_{H2}(T)$ and $\sigma_{C1}(T)$ overlap up to 600 K (see the Fig. 1). Above 630 K (650 K in some films), $\sigma_{H2}(T)$ branch increases its slope which keeps constant up to 700 K.

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[1] The pedix number refers to the cycle number.

[2] i.e. $\sigma_{Hn}(T) \simeq \sigma_{C1}(T)$, with *n* denoting the *n*-th thermal cycle ($n > 1$).