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The Meyer-Neldel rule in the conductivity of insulating germanium nitride and oxynitride films

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ABSTRACT

Electrical conductivity, $\sigma(T)$, of a-Ge_3N_x ($3.7 < x < 4.6$) and quasi-stoichiometric a-$Ge_2O_yN_x$ films has been investigated as a function of the temperature. Layers present a highly insulating behavior with conductivity and thermal activation energy rapidly rising, increasing T from room temperature to 600 K. Depending on the film composition, the conductivity can vary up to six orders of magnitude.

Data analysis of $\sigma(T)$ revealed a clear relation between the pre-exponential factor and the thermal activation energy, suggesting the validity of the Meyer-Neldel rule. For all investigated films, typical Meyer-Neldel parameters assume values in a narrow range: $10^{-8} < \sigma_{00} < 10^{-6}(\Omega\text{cm})^{-1}$ and $41 < E_{MN} < 51$ meV.

To account for this behavior we have considered a model based on a statistical shift of the Fermi level upon the temperature raise. Our study is the first experimental evidence of this kind of electrical behavior in this class of materials.

1. Introduction

Germanium based nitrides and oxynitrides, both in crystalline and amorphous phases, are insulators potentially interesting for 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. Ge_3N_4, with a band gap of $\simeq$4.5 eV, is a good candidate as a passivating layer for the fabrication of high performance and low leakage Ge $p-n$ junctions [5]. 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) [6].

Despite the interesting potential applications, the electronic transport properties of GeN and GeON based alloys are only partially known since the huge insulating properties of this class of materials represent 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 [7]. For these systems, experiments have demonstrated that insulating properties of Ge_3N_x, and Si_3N_x as well, deteriorate notably as the nitrogen concentration decreases far below $x \simeq 4$ [7]. To the authors best knowledge, studies and experimental data on the electronic transport properties of stoichiometric and over stoichiometric a-Ge_3N_x films are still missing.

In this work we have investigated the electrical conductivity as a function of T (above room temperature) of thin a-Ge_3N_x films, with $3.7 < x < 4.6$, deposited by reactive r.f. magnetron sputtering technique. Lowering the film deposition rate it has been possible to form a-$Ge_2O_yN_x$ layers with a composition near to the stoichiometry. Data analysis revealed that the conductivity pre-exponential factor of all studied a-Ge_3N_x and a-$Ge_2O_yN_x$ samples depends on the thermal activation energy and it fulfills the Meyer-Neldel rule (MNR). The observed features of the conductivity have been explained in terms of a phenomenological model based on the statistical shift of the Fermi level with the raise of T.

2. Experimental

Thin films of a-Ge_3N_x and a-$Ge_2O_yN_x$ have been deposited at room temperature (R.T.), by reactive r.f. magnetron sputtering by using a Ge target. Deposition has been carried out at a total gas flux of 40 sccm by using pure N_2 or an Ar+N_2 gas mixture (either at 20+20 sccm or 25+15 sccm of gas fluxes, respectively). Depending

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on the gas composition, the total pressure inside the chamber ranged from 12.7 mbar to 18.4 mbar, while the base pressure has been always lower than 10^{-6} mbar. The applied r.f. power and the target-substrate distance has been kept constant at 60 W and 5 cm, respectively, for a-Ge_3N_x films, and at 40 W and 14 cm, for a-$Ge_2O_yN_x$ films. A set of a-Ge_3N_x films has been deposited by r.f. biasing the samples, which acquired an average dc voltage from 0 V to −100 V, in step of −20 V.

In order to perform different physical analyses, diverse kinds of substrate (i.e. carbon, Si and sapphire) have been used simultaneously for each deposition run. Substrates have been chemically cleaned ex situ and have undergone a final in-situ ion-etching process of short duration before deposition.

Film stoichiometry has been analyzed by Rutherford backscattering spectrometry (RBS) by using a 2.0 MeV $^4He^+$ beam, at the Van der Graaf accelerator at the Laboratori Nazionali di Legnaro. Germanium, nitrogen and oxygen concentration has been determined at the scattering angle of 160°. RBS analysis has been performed on films deposited on vitreous carbon substrates. Films thickness has been measured by atomic force microscopy (AFM) on partially masked silicon substrates. Deposition parameters and the resulting film composition are reported in Table 1.

Electrical conductivity, $\sigma(T)$, of films deposited on sapphire substrates, was measured at dark in a co-planar contacts configuration, by using a small furnace operating in vacuum ($P < 10^{-5}$ mbar). Up to 4 Au circular pads were sputtered onto the film surface, near its borders. Au has been preferred to other metals or metal alloys, taking into account factors such as: mechanical adhesion of the metal to the film; mechanical and electrical stability upon thermal cycles; resistance to oxidation at high temperatures and ease deposition in vacuum. Other aspects such as the possible formation of a Schottky barrier and the electrical conductance, S, of the contact have been considered less relevant, due to the expected very low S values and then the need to use high applied bias to carry out the measurement. Current-voltage characteristics executed at several temperatures, between R.T. and 600 K, showed a linear behavior up to ±50 V (not reported here).

Due to the extremely low S values detected at R.T., we were forced to execute all the measurements in the two contacts geometry, by using an electrometer (Keithley either mod. 617 or 6517B) operating in the V/I mode, i.e. applying a constant bias and measuring the current. Depending on the R.T. conductance, the applied bias ranged from 10 V to 100 V, with a typical value of 50 V. An upgrade in the insulation resistance of the measuring apparatus, has allowed to extend the sensitivity of the measure of about one order of magnitude.

To avoid any data misunderstanding, we have systematically checked the insulation of the whole measuring apparatus, at several fixed T. Typical insulation of our apparatus, after the upgrade, has been $\approx 10^{-15}\Omega^{-1}$ from R.T. to about 600 K, falling down to $\approx 10^{-12}\Omega^{-1}$ around 700 K. These values have been considered as the lowest possible limit for the S values measured in our films. Hence, due to this limitation, the real $\sigma(T)$ of several films has resulted unmeasurable around R.T., and in some layers even up to ≈450 K.

Thermal energy in the film has been changed very slowly, with a rate of about 0.5 ÷ 1 K/min and $S(T)$ collected after T stabilization to better than 1 K (typically 0.5 K). For every T, 25 ÷ 30 $S(T)$ values have been averaged to calculate the corresponding $\sigma(T)$ value.

3. Results

For the electrical characterization, all films have undergone a thermal cycle, from R.T. up to 600 K and then back to R.T., and the conductivity has been measured without any break during the heating and the cooling run. During the first cycle, the conductivity measured during the heating, $\sigma_H(T)$, has assumed values higher than those measured in the cooling run, $\sigma_C(T)$, due to the film exposure to the ambient air [7,8]. This effect has disappeared repeating the measurement under the same conditions, without breaking the vacuum. Data analysis has been done taking into account only the $\sigma_C(T)$ curves.

A set of investigated films has been deposited under the same nominal conditions, except for the average dc voltage acquired by the r.f. biased sample, hereafter referred as bias (Table 1). A striking effect of the bias has been the lowering of the a-Ge_3N_x film stoichiometry, proportionally to the bias value, from $x = 4.6$ (at 0 V) to $x = 3.8$ (at −100 V), which points to a preferential re-sputtering of nitrogen with respect to germanium, as induced by ion bombardment during film growth. We have found that at zero bias the addition of Ar to N_2 during the deposition, while keeping the a-Ge_3N_x composition near the stoichiometry ($x \approx 4$: *#G* and *#H*, Table 1), improves the insulation properties of films, as will be shown later. On the other hand, lowering the deposition rate of about one order of magnitude, under the same conditions, has resulted in the formation of practically stoichiometric a-$Ge_2O_yN_x$ layers (i.e. *#I* and *#L*) due to oxygen contamination by the residual water vapor present in the deposition chamber [9].

The S value detected at R.T. (except for film *#F*) results comparable to the insulation conductance of the measuring apparatus, suggesting that the effective S value of films could be even lower. Hence, the knowledge of the R.T. conductivity has been prevented for all samples but *#F*. For all the other layers, it has been possible to measure $\sigma_C(T)$ only at $T \gtrsim 350 \div 450$ K, the minimum T depending on the film properties (Fig. 1). Samples *#B*, *#C* and *#G* have been characterized before the upgrade of the measuring setup, which resulted in a $\sigma_C(T)$ curve starting at a higher T value. Finally, for a technical problem occurred during the measurement, the conductivity of the film *#H* was carried out up to ≃520 K.

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; Film stoichiometry; bias (the average dc voltage acquired by the r.f. biasing of the sample); Gas mixture and relative flow; Film thickness (by AFM); Ge surface density; Total deposition rate of the film. 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	Bias (V)	Gas/Flux (sccm)	Thickness (nm)	n_{Ge} (at/cm^2)	V_{dep} (Ge_{at}/s • cm^2)
#A	$Ge_3N_{4.6}$	0	N_2, 40	124	4.3×10^{17}	1.0×10^{15}
#B	$Ge_3N_{4.6}$	−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}
#D	$Ge_3N_{4.1}$	−60	N_2, 40	181	6.3×10^{17}	1.0×10^{15}
#E	$Ge_3N_{4.1}$	−80	N_2, 40	159	5.5×10^{17}	9.3×10^{14}
#F	$Ge_3N_{3.7}$	−100	N_2, 40	160	5.5×10^{17}	8.8×10^{14}
#G	$Ge_3N_{4.1}$	0	N_2+Ar, 20+20	217	7.5×10^{17}	1.7×10^{15}
#H	$Ge_3N_{4.1}$	0	N_2+Ar, 15+25	261	9.1×10^{17}	2.0×10^{15}
#I	$Ge_2O_{1.2}N_{1.9}$	0	N_2+Ar, 20+20	127	4.4×10^{17}	1.6×10^{14}
#L	$Ge_2O_{1.2}N_{1.9}$	0	N_2+Ar, 20+20	43	1.5×10^{17}	1.6×10^{14}