Applied Surface Science 393 (2017) 119–126

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Germanium nitride and oxynitride films for surface passivation of Ge radiation detectors

G. Maggioni[a,b,*], S. Carturan[a,b], L. Fiorese[b,c], N. Pinto[d,e], F. Caproli[d,e], D.R. Napoli[b], M. Giarola[f], G. Mariotto[f]

[a] Dipartimento di Fisica e Astronomia G. Galilei, Università di Padova, Via Marzolo 8, I-35131 Padova, Italy
[b] Laboratori Nazionali di Legnaro, Istituto Nazionale di Fisica Nucleare, Viale dell'Universita'2, I-35020 Legnaro, Padova, Italy
[c] Dipartimento di Ingegneria dei Materiali e delle Tecnologie Industriali, Università di Trento, Via Mesiano 77, I-38050 Povo, Trento, Italy
[d] Scuola di Scienze e Tecnologie, Sezione di Fisica, Università di Camerino, Via Madonna delle Carceri 9, Camerino, Italy
[e] INFN, Sezione di Perugia, Perugia, Italy
[f] Dipartimento di Informatica—Università di Verona, Strada le Grazie 15, I-37134 Verona, Italy

ARTICLE INFO

Article history:
Received 6 June 2016
Received in revised form 9 September 2016
Accepted 2 October 2016
Available online 4 October 2016

Keywords:
Germanium nitride layer
Germanium oxynitride layer
Room temperature deposition
Electrical resistivity
Surface passivation
Hyperpure germanium detector

ABSTRACT

This work reports a detailed investigation of the properties of germanium nitride and oxynitride films to be applied as passivation layers to Ge radiation detectors. All the samples were deposited at room temperature by reactive RF magnetron sputtering. A strong correlation was found between the deposition parameters, such as deposition rate, substrate bias and atmosphere composition, and the oxygen and nitrogen content in the film matrix. We found that all the films were very poorly crystallized, consisting of very small Ge nitride and oxynitride nanocrystallites, and electrically insulating, with the resistivity changing from three to six orders of magnitude as a function of temperature. A preliminary test of these films as passivation layers was successfully performed by depositing a germanium nitride film on the intrinsic surface of a high-purity germanium (HPGe) diode and measuring the improved performance, in terms of leakage current, with respect to a reference passivated diode. All these interesting results allow us to envisage the application of this coating technology to the surface passivation of germanium-based radiation detectors.

1. Introduction

Germanium (Ge) has recently aroused renewed interest in microelectronics owing to its higher hole and electron mobilities as compared to silicon (Si) [1], while its high absorption coefficient in optical communication bands makes it a good candidate for the development of Ge optical devices [2].

One of the most serious issues in the fabrication of Ge devices concerns the passivation of Ge surfaces. Differently from Si, Ge forms unstable oxides: GeO_2 is water-soluble and decomposes under thermal treatment around 420 °C [3] so that it cannot be used in wet processes and thermal treatments in ULSI fabrication processes [4]. For this reason, alternative passivation coatings have been studied and developed and several Ge-based dielectric compounds (such as Ge nitrides and oxynitrides) are now considered potentially interesting for technological applications. In particular, germanium nitride (Ge_3N_4) exhibits a high dielectric constant, is water-insoluble and its thermal decomposition temperature is higher than GeO_2 [5,6] so that it could be applied not only as a buffer layer for high-k dielectrics grown on Ge substrates but also for the passivation of Ge surfaces. Germanium oxynitrides (GeO_xN_y) are also promising materials, because nitrogen incorporation in GeO_2 has proven to improve its chemical and thermal stability [7]: the decomposition temperature of a GeO_xN_y layer was found to increase up to 550 °C, which was more than 100 °C higher than that of pure GeO_2 [8,9].

A key role to tailor the passivating properties of this class of materials is played by the deposition technique. Germanium nitride and oxynitride layers are usually grown by techniques such as thermal and plasma nitridation of Ge surfaces [4,3,10], chemical vapor deposition [11] and thermal ammonolysis of GeO_2 [12,13]. Reactive sputtering technique, using N_2, NH_3 or N_2H_4 as reactive gas, has been also exploited for the deposition of germanium nitride layers [14–18]. These techniques usually require heating the substrate up to some hundreds of Celsius degrees during the film growth in order

* Corresponding author at: Dipartimento di Fisica e Astronomia G. Galilei, Università di Padova, Via Marzolo 8, I-35131 Padova, Italy.
E-mail address: maggioni@lnl.infn.it (G. Maggioni).

http://dx.doi.org/10.1016/j.apsusc.2016.10.006
0169-4332/

Table 1
Deposition parameters of germanium nitride and oxynitride films. Ge deposition rate and film composition were determined by RBS. The errors on the N and O values are around 5%.

Sample	Target-substrate distance (cm)	RF power (W)	Sample DC Bias (V)	Gas composition	Gas flow (sccm)	Ultimate pressure (Pa)	Water vapor bombardment rate (10^{13} molecules cm^{-2} s^{-1})	Ge deposition rate (10^{13} atoms cm^{-2} s^{-1})	Film composition
A	14	40	–	N_2	40	8.5×10^{-5}	3.1	10.7	$Ge_2O_{1.0}N_{2.1}$
B	5	60	–	N_2	40	4.1×10^{-5}	1.5	104	$Ge_3N_{4.6}$
C	5	60	–	N_2:Ar	25:15	3.4×10^{-5}	1.2	184	$Ge_3N_{4.0}$
D	14	40	–	N_2:Ar	20:20	8.6×10^{-5}	3.1	15.8	$Ge_2O_{1.2}N_{1.9}$
E	5	60	–	N_2:Ar	20:20	3.3×10^{-5}	1.2	171	$Ge_3N_{4.1}$
F	5	60	–	N_2:Ar	15:25	3.4×10^{-5}	1.2	197	$Ge_3N_{4.1}$
G	5	60	−20	N_2	40	1.1×10^{-4}	4.0	104	$Ge_3N_{4.6}$
H	5	60	−40	N_2	40	3.8×10^{-4}	13.7	103	$Ge_3N_{4.2}$
I	5	60	−60	N_2	40	1.1×10^{-4}	4.0	103	$Ge_3N_{4.1}$
J	5	60	−80	N_2	40	1.4×10^{-4}	5.1	93	$Ge_3N_{4.1}$
K	5	60	−100	N_2	40	1.9×10^{-4}	6.8	88	$Ge_3N_{3.7}$

to promote the reaction between germanium and nitrogen/oxygen species. This requirement can be a drawback for those applications, where the substrate can be damaged by an excessively high temperature. This is the case when the germanium (oxy)nitride coating has to be applied as a passivation layer to the intrinsic surface of a high-purity Ge (HPGe) detector [19–21]. In fact, an excessive heating can promote the unwanted diffusion of contaminant species and of Li atoms (used for the n^+ contact of Ge detectors) then jeopardizing the detector performance.

Aiming at this specific application, in this work we optimized the room temperature (R.T.) deposition of germanium nitride and oxynitride films by means of reactive RF magnetron sputtering as a technique for producing passivation coatings for Ge-based devices.

Several films were prepared under different deposition parameters, such as atmosphere composition and deposition rate, and their main physical properties were characterized. One set of films was obtained by RF biasing the substrates, in order to study the effects of the ion bombardment on the film properties.

As a final step of our study, a germanium nitride coating was deposited onto the intrinsic surface of a planar HPGe diode and the reverse leakage current of the biased diode, with and without coating, was measured and compared.

2. Experimental details

The experimental equipment used for the coatings deposition consisted of a stainless steel vacuum chamber evacuated by a turbomolecular pump to a base pressure lower than 5×10^{-4} Pa. The glow discharge sustaining device was a 2-in. cylindrical magnetron sputtering source connected to a radio frequency power generator (600 W, 13.56 MHz), through a matching box. All films were deposited at two values of the RF power: 40 W and 60 W. Pure Ge (99.999%) was used as a target. Several N_2-Ar gas mixtures were used for the depositions (see Table 1) by regulating the gas flow of each gas. The different substrates (silicon, carbon and sapphire) were placed on a sample holder at distances of 5 cm and 14 cm.

A set of films was prepared by biasing the samples with a second RF power generator (600 W, 13.56 MHz), which resulted in an average dc voltage acquired by the samples and purposely fixed at values ranging from 0 V to −100 V, in step of −20 V. In this way, a controlled ion-bombardment-assisted deposition was achieved at a constant average ion energy. The time for each deposition run was varied in order to achieve a film thickness between 100 and 300 nm. For Raman spectroscopy measurements, the deposition times were extended in order to get 600 nm thick samples. A mass spectrometer (Prisma Plus QMG 220, Pfeiffer Vacuum) revealed water vapor as the main residual component in the deposition chamber.

Rutherford Backscattering Spectrometry (RBS) was performed using 2.0 MeV $^4He^+$ beam at the Van de Graaf accelerator at the Laboratori Nazionali di Legnaro, at the scattering angle of 160°, in order to determine film deposition rate and composition. Samples were characterized 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° incidence using CuK_α Ni filtered radiation at 40 kV and 40 mA.

The vibrational dynamics of germanium nitride samples was probed by either FT-IR or Raman 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}. Micro-Raman spectra were carried out in backscattering geometry, at room temperature, under excitation at 514.5 nm or, alternatively, at 647.1 nm by means of a triple-axis monochromator (Horiba-Jobin Yvon, model T64000), set in double-subtractive/single configuration, and equipped with holographic gratings having 1800 lines/mm. The scattered radiation was detected by a charge coupled device detector, with 1024×256 pixels, cooled by liquid nitrogen, and the spectral resolution was better than 0.6 cm^{-1}/pixel. All the spectra were calibrated in frequency using the emission lines of an Ar spectral lamp.

The surface morphology of the samples was investigated either by a SEM (Tescan Vega3 XM) equipped with the energy dispersive spectrometry (EDS) option or by a no-contact-mode AFM model C-21 (Danish Micro Engineering), mounting a DualScope Probe Scanner 95-50.

Electrical resistivity, $\rho(T)$, of films deposited on sapphire substrates was measured in a co-planar configuration as a function of the temperature from about 300 K–600 K, by using a small furnace operating in vacuum ($P < 10^{-3}$ Pa) and at dark. Four Au electrodes, about 5 mm apart, were sputtered on the film surface, near its borders. Due to the extremely high resistance exhibited by all the films, the measurements were carried out in a two contacts geometry, by using electrometers (Keithley either mod. 617 or 6517 B) operating in the V/I mode. During this work the experimental setup was updated in order to measure higher values of the sample resistance. Depending on the room temperature resistance, the applied bias ranged from 10 V to 100 V, with a typical value of 50 V. Thermal energy in the film was changed very slowly, with a rate of about 0.5–1 K/min and $\rho(T)$ collected after T stabilization to better than 1 K (typically 0.5 K). Each $\rho(T)$ value was obtained averaging 25–30 data points, collected at a fixed T value. Film resistivity was measured continuously, from room temperature (R.T.) up to 600 K and then back to R.T.

A planar, cylindrical HPGe diode of 19 mm (height) × 39 mm (diameter) was prepared in our laboratory to check the passivation properties of germanium nitride coatings. The p^+ contact was