Thin Solid Films 599 (2016) 49–53

Contents lists available at ScienceDirect

Thin Solid Films

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

Controllable growth of stable germanium dioxide ultra-thin layer by means of capacitively driven radio frequency discharge

P. Svarnas [a],*, M.A. Botzakaki [b], G. Skoulatakis [c], S. Kennou [c], S. Ladas [c], C. Tsamis [d], S.N. Georga [b], C.A. Krontiras [b]

[a] High Voltage Laboratory, Department of Electrical and Computer Engineering, University of Patras, Rion 26 504, Patras, Greece
[b] Department of Physics, University of Patras, Rion 26 504, Greece
[c] Surface Science Laboratory, Department of Chemical Engineering, University of Patras, Rion 26 504, Greece
[d] NCSR "Demokritos", Institute of Advanced Materials, Physicochemical Processes, Nanotechnology & Microsystems, Aghia Paraskevi 15 310, Athens, Greece

ARTICLE INFO

Article history:
Received 23 June 2015
Received in revised form 21 December 2015
Accepted 22 December 2015
Available online 23 December 2015

Keywords:
Germanium oxidation
Reactive ion etcher
High-k dielectrics
MOS devices

ABSTRACT

It is well recognized that native oxide of germanium is hygroscopic and water soluble, while germanium dioxide is thermally unstable and it is converted to volatile germanium oxide at approximately 400 °C. Different techniques, implementing quite complicated plasma setups, gas mixtures and substrate heating, have been used in order to grow a stable germanium oxide. In the present work a traditional "RF diode" is used for germanium oxidation by cold plasma. Following growth, X-ray photoelectron spectroscopy demonstrates that traditional capacitively driven radio frequency discharges, using molecular oxygen as sole feedstock gas, provide the possibility of germanium dioxide layer growth in a fully reproducible and controllable manner. Post treatment ex-situ analyses on day-scale periods disclose the stability of germanium oxide at room ambient conditions, offering thus the ability to grow (ex-situ) ultra-thin high-k dielectrics on top of germanium oxide layers. Atomic force microscopy excludes any morphological modification in respect to the bare germanium surface. These results suggest a simple method for a controllable and stable germanium oxide growth, and contribute to the challenge to switch to high-k dielectrics as gate insulators for high-performance metal-oxide-semiconductor field-effect transistors and to exploit in large scale the superior properties of germanium as an alternative channel material in future technology nodes.

1. Introduction

Germanium is one of the most important semiconductors for electronics due to its intrinsic high mobility of electrons and holes, small band gap leading to lower contact resistances because of reduced barrier height, and easy integration on silicon [1]. Conversely, one of the main disadvantages is the instability of the germanium oxides (GeO_x). This instability remains one of the key enablers in different applications, such as Ge-based metal-oxide-semiconductor field-effect transistor (MOSFET) gate insulation and integrated-circuit isolation.

Native oxides of germanium are hygroscopic and water soluble, with their nature and thickness being history dependent. Germanium dioxide (GeO_2) is thermally unstable and it is converted to volatile germanium monoxide (GeO) [1]. Ultra-high vacuum experiments show that the adsorption of atomic oxygen takes place already at room temperature, with the prevailing formation of sub-oxide species [2]. In this latter report, when the oxidation temperature was fixed at 300 °C, the oxide layer was primarily GeO_2. GeO_2 was stable up to 400 °C while a severe decomposition took place when the annealing temperature reached 500 °C. Additionally, annealing experiments on the oxide formed at room temperature revealed that for temperatures ranging from 450 °C to 475 °C the minority GeO_2 was transformed into sub-oxide species, which in turn were desorbed upon a further increase of the annealing temperature up to 500 °C [2]. Thus, the interest in Ge as a channel material for nanoscale MOSFETs could be justified in practice, if a stable as well as scalable gate technology could be developed. A main approach that has shown to hold promises towards this direction is the formation of an electrically insulating pad, between the gate and the doped germanium, consisting of a GeO_2 interfacial passivating layer and a high-k dielectric layer onto that [3], thus maintaining a low equivalent oxide thickness.

In order to meet this concept, GeO_2 dielectric growth by several techniques has been attempted, including wet chemical oxidation [4], thermal oxidation [5,6], vacuum ultraviolet-assisted oxidation at temperature lower than 450 °C [7], and ozone oxidation at 15 Torr under 200–450 °C [8], just to name a few. Additionally, plasma-based oxidation has also been tested. Electron cyclotron resonance (ECR) source (2.45 GHz/500 W for oxidation and additionally 13.56 MHz/500 W for sputtering deposition) operating with argon and molecular oxygen gases has been used [9,10]. The sample was not externally heated but its temperature was risen up to about 100 °C and it was placed in an extracting (remote) region, while high-k dielectric deposition was

---

* Corresponding author.
E-mail address: svarnas@ece.upatras.gr (P. Svarnas).

http://dx.doi.org/10.1016/j.tsf.2015.12.049

carried out in-situ following oxidation. In another approach, ECR-induced Ge oxidation through the thin high-k deposited layer, i.e. post oxidation, was considered [11]. Inductively coupled plasma (ICP) in a downstream configuration has also been employed for germanium oxidation and subsequent in-situ growth of high-k dielectric by plasma-enhanced atomic layer deposition. The substrate was maintained at 250 °C and the RF power applied was less than 600 W [1,12,13].

Unlike to the aforementioned techniques where substrate heating, quite complicated plasma setups, gas mixtures or in-situ deposition of high-k dielectrics are indispensable, a traditional "RF diode" [14] is suggested in the present work as an effective medium for germanium oxidation by cold plasma. The system comprises a simple capacitively driven radio frequency reactor housing two electrodes of plane parallel geometry. O_2 is used as single feedstock gas and the substrate remains to low temperature (<100 °C). The bare and plasma-treated Ge surfaces are probed by X-ray photoelectron spectroscopy (XPS). The formation of an ultra-thin GeO_2 layer between 0.45 and 3.2 nm is achieved, with its thickness being reproducibly dependent on the plasma exposure time. Post-treatment ex-situ XPS analyses on day-scale periods disclose the stability of this passivating layer even when a high-k dielectric such as hafnium dioxide (HfO_2) is superimposed by means of atomic layer deposition (ALD). In parallel, atomic force microscopy (AFM) excludes any morphological modification in respect to the bare germanium surface. Following these results, the applicability of the proposed technique for obtaining improved MOS structures is proven here in practice. It is underlined that the present work claims on the existence of a simple low-temperature method for stable GeO_2 formation preventing substrate damage, and it is not devoted to the well known potentiality of Ge as a candidate for Si replacement in future electronic devices.

2. Experimental setups and materials

Germanium substrates were supplied from Umicore Inc. They were Czochralski grown p-type Ge substrates with 0.04–0.4 Ω cm resistivity. Prior to plasma exposure, the substrates were chemically cleaned in order to remove the native oxide and organic residues, following conventional cleaning procedure [15–17].

Surface oxidation of Ge substrates, was then carried out by a plasma-based process. A reactive ion etcher (RIE) of parallel plate (150 mm in diameter) electrode configuration was used. The top electrode was grounded directly and the bottom one was biased by standard radio frequencies (13.56 MHz). This driven electrode was shielded, thus confining the plasma in the inter-electrode gap (50 mm) as much as possible [18,19]. The sample was placed in a groove ($20 \times 20 \times 1$ mm^3) machined on a detachable part (holder) of the driven electrode. The system was equipped with load-lock assembly and long axial vacuum manipulator of the holder, for increased sample throughput. The base pressure in the processing chamber was 4×10^{-5} Torr. The working pressure for the present study was 30 mTorr of high purity O_2, with the gas being introduced into the chamber with a vertical flow of 50 sccm. The driving power (as read on the RF-generator integrated wattmeter) was 45–50 W (reflected power less than 2 W). In this work, Ge substrates were exposed to O_2 plasma for increasing time intervals from 5 to 300 s.

The bulk plasma was probed by means of spatially-integrated UV–visible high resolution optical emission spectroscopy (HR-OES), using a monochromator (Jobin Yvon THR 1000, 170–750 nm, 2400 grooves/mm) equipped with photoelectron multiplier tube (Hamamatsu R928, 185–900 nm) and optical fibre (Ceramoptec UV 1500/1590 N). All the optical components were calibrated in terms of relative spectral efficiency, using a quartz-tungsten-halogen lamp operated at 3300 K. The average gas temperature was thus estimated approximately, by fitting theoretical rotational distributions of probe molecules to the experimentally determined distributions [20].

Hafnium dioxide (HfO_2) films were developed by means of atomic layer deposition technique (Nanotech Savannah, 100 ALD system, Cambridge, USA) at 200 °C, using tetrakis(dimethylamido)hafnium [$Hf(NMe_2)_4$] (heated at 75 °C) as precursor and water as the co-reactant. HfO_2 thin films were grown by a series of 33 repetitive cycles, each one consisting of $Hf(NMe_2)_4$ and H_2O precursors pulsed for 0.15 s and 0.015 s, respectively. Each pulse was followed by a 25 s time interval of N_2 purging at a flow rate of 20 sccm. Thus, the HfO_2 layers were deposited through a double-exchange chemical reaction of the form [21]:

$$Hf[N(CH_3)_2]_4 + 2H_2O \rightarrow HfO_2 + 4HN(CH_3)_2.$$

According to the ALD system specifications, the repetition of 33 cycles produces HfO_2 films with nominal thickness of 3 nm. However, the actual thickness of the grown films was tested through XPS.

For the electrical characterization of the samples, Au-MOS capacitive structures were developed using standard photo-lithography and lift-off processes. The back ohmic contact was formed through eutectic In-Ga alloy. In order to perform the electrical measurements, the samples were mounted in a cryogenic probe station (MDC 411H). C–V and C–f measurements were performed at room temperature by AC impedance spectroscopy, using a Novocontrol Alpha-N Dielectric Response Analyzer suitably controlled by the WinDeta software. J–V measurements were also performed at room temperature, using Keithley 2611A system SourceMeter. They were carried out in the range between 0.0 and 1.0 V, under forward and reverse bias voltages. The forward bias condition corresponded to the case of negative biasing on the top Au electrode.

The plasma-treated Ge samples were characterized ex-situ by XPS using the unmonochromatized Al Kα line at 1486.6 eV (12 kV with 20 mA anode current) and a Leybold EA-11 analyzer with pass energy of 100 eV. In all measurements, the C1s binding energy at 285.0 eV was used as a reference for the binding energy scale.

Surface topography images were obtained using AFM at the tapping mode with the constant force method. The samples were imaged with the aid of a MultiMode Scanning Probe Microscope (Bruker), using a Nanoscope IIIa controller and a 120×120 μm^2 magnet-free scanner (ModelAS-130VMF) with vertical range 5 μm and z-axis resolution 0.05 nm. The images were processed with a linear plane fit in order to remove any sample tilt appeared on them [22].

3. Results and discussions

Fig. 1 presents the Ge 3d XPS peak of a cleaned Ge substrate after 60 s of plasma treatment. Ge 3d appears in two main components; one at a binding energy of 29.7 eV, which originates from the substrate Ge(0), and another one shifted by about 3.3 eV towards higher

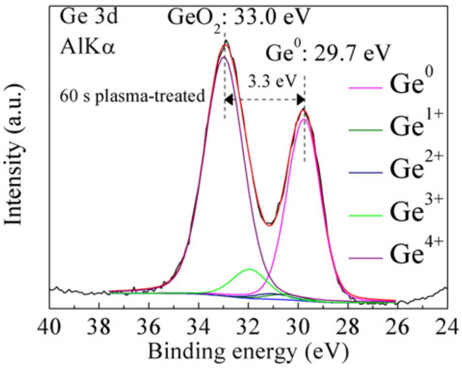

Fig. 1. Typical Ge 3d X-ray photoelectron spectroscopy peak for a 60 s plasma-treated Ge substrate, with the various components identified.