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Thin Solid Films

Metal-insulator-SiC Schottky structures using $HfO₂$ and TiO₂ dielectrics

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ARTICLE INFO ABSTRACT

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Metal-Insulator-Semiconductor Schottky diodes were fabricated on SiC, as a potential use for particle detectors. Nickel was used as Schottky and back ohmic contacts. The dielectrics HfO₂ and TiO₂ were investigated as insulating layers and deposited by Atomic Layer Deposition, with thicknesses of 1, 2 and 4 nm. Current-Voltage curves were extracted from the diodes, varying the measurement temperature (297 K–373 K). Apparent and real Schottky Barrier Heights (SBH_{apparent} and SBH_{real}), ideality factor η and insulating layer thicknesses were extracted from the I-V curves. Thicker insulating layers produce higher η and reduce the SBH_{real} value, for both dielectrics. An interfacial layer of silicon oxycarbide with thickness of 0.2 nm was estimated for all diodes. The SBH_{real} goes from 1.22 V to 0.66 V and from 1.26 V to 0.59 V, for thicknesses of 1 nm and 4 nm of HfO₂ and TiO₂, respectively. The reverse currents for all structures at 40 V of bias are of order of tens of pA at room temperature. © 2016 Elsevier B.V. All rights reserved.

1. Introduction

SiC is a semiconductor with wide bandgap (3.27 eV), high thermal conductivity (4.9 W cm⁻¹ K⁻¹), high-breakdown field strength (4 MV cm⁻¹), high electron saturated drift velocity (2 \times 10⁷ cm s⁻¹) and high threshold displacement energy (22–35 eV) [\[1,2\]](#page--1-0). These properties make SiC suitable to be used in extreme conditions such as high-temperature (573–873 K), high-power, high-frequency, high radiation background and hot environments [\[3,4\]](#page--1-0).

When SiC is compared to other traditional semiconductors (like silicon, germanium and gallium arsenide), the characteristics listed previously provide a lighter and more compact device, which can operate for long periods of time in extreme environments without varying its physical and chemical proprieties, [\[1,5,6\].](#page--1-0) To be used as a particle detector, SiC presents the advantage of being more resistant to radiation. This means that the SiC detector's parameters are very little affected by exposure to radiation [\[1,7](#page--1-0)–9].

One concern is regarding the choice of the metal to form the Schottky contact. This contact must provide two important characteristics: high Schottky Barrier Height (SBH) and minimum reverse current. These two diode characteristics are correlated, since the reverse current depends on the height of the Schottky barrier [\[10\].](#page--1-0)

In particular, SiC Schottky devices always have a thin insulating film of native silicon oxycarbide (SiC_xO_y) between metal and SiC [\[11,12\].](#page--1-0) Many attempts to completely remove these components in wet environments were unsuccessful, evidencing their high chemical resistance [\[13\]](#page--1-0). So, the traditional Schottky contact between metal and SiC became

Corresponding author. E-mail address: ivanrodrigo.kaufmann@gmail.com (I.R. Kaufmann). closer to a Metal-Insulator-Semiconductor (MIS) structure. A MIS Schottky structure can present better electrical characteristics compared to traditional Metal-Semiconductor (MS) junctions, when the issue is reverse biased detector. The reason for the poorer electrical characteristics of the MS structures is the strong Fermi-level pinning, related to metal-induced gap states located at the MS interface [\[14,15\].](#page--1-0) This problem has been alleviated with the insertion of a thin interfacial layer, that can simultaneously unpinning the Fermi-level and offer an additional quantum barrier to carriers when the detector is reverse biased [\[16,17\]](#page--1-0). For thicknesses smaller than 5 nm, tunneling through the insulator is possible [\[10,18\]](#page--1-0).

In a previous study [\[19\]](#page--1-0) we have shown that SBH increases with the increase of the measuring temperature of the Current-Voltage (I-V) experiments, due to the existence of thin insulating films between metal and semiconductor in a Schottky structure. In the present work, we investigate the influence of $HfO₂$ and TiO₂ thin layers deposited onto SiC, before the metal deposition, with potential use in particle detectors.

2. Experimental details and Schottky parameters extraction

SiC Schottky structures were fabricated on 4H-SiC (n-type) commercial epitaxial wafers, 8° off-axis on the Si face, doped with nitrogen $(1 \times 10^{15} \text{ cm}^{-3})$ and 6 µm thick. The wafers were purchased from CREE Inc. Research. All substrates were cleaned in a mixture of $H₂SO₄$ and H_2O_2 followed by the standard RCA process. Then the samples were etched for 60 s in a 1 vol.% aqueous solution of hydrofluoric acid (40 wt.% HF, purchased from Merck), rinsed in deionized water and dried with N_2 . A layer of Ni with a thickness of 300 nm was deposited by sputtering on the SiC wafers (non-polished face). The backside

ohmic contacts were formed in a Rapid Thermal Annealing (RTA) lamp system in an argon flow at 1223 K for 5 min.

Hafnium dioxide (HfO₂) and titanium dioxide (TiO₂) were deposited by Atomic Layer Deposition (ALD), with nominal thicknesses of 1, 2 and 4 nm. ALD was performed using a Beneq TFS200 reactor, with deposition rate of 0.0833 nm/cycle and 0.025 nm/cycle, for $HfO₂$ and TiO₂, respectively.

A SOPRA GES-5E Spectroscopic Ellipsometer was used in the film characterization. All measurements were done at an angle of incidence of 75°, in the wavelength range of 0.25 μm to 0.8 μm. To perform the fitting to experimental data and obtain the film thickness, a Cauchy's model [\[20\]](#page--1-0) was used for dispersion curve (the films were assumed as homogeneous and isotropic). All thickness measurements were estimated within a 5% error of the nominal thickness.

The front contacts were fabricated by sputtering of Ni through a mechanical mask, forming circular electrodes with a diameter of 1.1 mm and thickness of 300 nm. A second RTA was performed in argon at 673 K for 5 min for Schottky contacts improvement [\[21\].](#page--1-0)

The samples were electrically characterized by I-V measurements at different temperatures, using an HP4155A Semiconductor Parameter Analyzer. Simulation with the "Band Diagram Program", v.2.1.5.9 [\[22\],](#page--1-0) developed by Knowlton Research Group of Boise State University, was used to extract the interfacial layer effective barriers (ζ) of the insulating layers.

To extract information about the SBH from Schottky diodes, the Thermionic Emission (TE) model is widely used [\[21,23,24\]](#page--1-0). Normally, the apparent SBH and the ideality factor η are extracted using the following equations [\[10,21\]:](#page--1-0)

$$
J = A^* T^2 \exp\left(-\frac{q\Phi_{SBH(\text{apparent})}}{kT}\right) \left[\exp\left(\frac{qV}{\eta kT}\right) - 1\right]
$$
 (1)

$$
\eta = \frac{q}{kT} \frac{dV}{d(lnJ)},\tag{2}
$$

where J is the current density ($A/cm²$), A^* is the effective Richardson constant, T is the temperature of measurement, q is the electron charge, k is the Boltzmann constant, V is the applied bias and $\phi_{SBH(apparent)}$ is the apparent SBH.

However, when considering MIS structures, the traditional equation of TE must take into account the insulating layers present in the Schottky structures. In this case, the current density is a function of the applied voltage, given by the equation [\[10,19\]:](#page--1-0)

$$
J = A^* T^2 \exp\left(-\sqrt{\zeta_1} \delta_1 - \sqrt{\zeta_2} \delta_2\right)
$$

$$
\exp\left(-\frac{q\Phi_{SBH(\text{real})}}{kT}\right) \left[\exp\left(\frac{qV}{\eta kT}\right) - 1\right].
$$
 (3)

Eq. (3) considers a MIS structure with two insulating layers. δ and $ζ$ are the layers thickness and effective barrier, respectively. The indices 1 and 2 represent the two different insulators: one is the deposited insulating layer and the other is the native $\text{SiC}_{x}\text{O}_{y}$.

Eq. (3) cannot be directly used to extract $\phi_{SBH (real)}$, because information for δ_1 and δ_2 is necessary. By combining Eqs. (1) and (3) one can calculate:

$$
\phi_{SBH (apparent)} = \phi_{SBH (real)} + \frac{kT}{q} \left(\sqrt{\zeta_1} \delta_1 + \sqrt{\zeta_2} \delta_2 \right), \tag{4}
$$

where $\phi_{SBH (real)}$ does not depend on the temperature, but ϕSBH(apparent) depends linearly.

In the case when only one dielectric layer is present in the MIS structure, one can measure $\phi_{SBH(\text{apparent})}$ as a function of the temperature and calculate the thickness δ of the layer, using ζ from the literature. For two different dielectric layers, the only way is to take into account the ratio between deposited nominal thicknesses and calculate the true values using two equations with two variables.

3. Results and discussion

Forward I-V characteristics of MIS diodes containing $HfO₂$ with thicknesses of 1, 2 and 4 nm are presented in Fig. 1. These curves are used to extract the Schottky parameters ($ln J \times V$). As the HfO₂ thickness increases, the forward current decreases. This is mainly because of two reasons [\[24\]:](#page--1-0) (i) the electrons have to tunnel through the barrier presented by the insulator and (ii) a part of the voltage applied on the metal is dropped across the insulating layer. The second reason produces a SBH dependence on the applied bias and shifts the I-V curves to higher voltages, for thicker insulating layers.

[Fig. 2](#page--1-0) shows the SBH (a) and the ideality factor η (b) as functions of the I-V curves measurement temperatures, for nominal thicknesses of 1, 2 and 4 nm of $HfO₂$. As mentioned previously, the nominal thicknesses were confirmed with ellipsometry and showed a variance of less than 5% from one diode to another (in all dielectric depositions from this study). The $\phi_{SBH(apparent)}$ values were calculated using Eq. (4) (extrapolating to 0 K), with values of 1.22, 1.11 and 0.66 V, for the diodes with 1, 2 and 4 nm, respectively. The SBH presented a variance of less than 4% from one diode to another, for the diodes with nominal thickness of 1 and 2 nm from the same sample. The diodes with thickness of 4 nm presented SBH variance higher than 10%. Thicknesses of more than 4 nm did not present Schottky characteristics. These diodes are closer to a MOS than to a MIS structure.

The apparent SBH versus temperature presents a good linear dependence, evidencing good Schottky characteristics. [Fig. 2](#page--1-0)b) shows η as a function of measurement temperature. The ideality factor increases for thicker insulating layers. The diode with nominal thickness of 1 nm of HfO₂ presented η close to unit, evidencing that the I-V current is generated mainly by TE. The diodes with nominal thicknesses of 2 nm and 4 nm of HfO₂ presented η of 1.2 and 1.65, respectively.

[Table 1](#page--1-0) presents the insulator thicknesses extracted using Eq. (4). A native $\text{SiC}_{x}\text{O}_{y}$ with thickness around 0.2 nm was inferred for the diodes. The nominal thicknesses of 1, 2 and 4 nm are in close accordance with those calculated through Eq. (4): 1.12, 2.24 and 4.37 nm, respectively.

Structures with $TiO₂$ deposited by ALD were also prepared to be investigated as Schottky MIS diodes. [Fig. 3](#page--1-0) shows the apparent SBH and the ideality factor η as functions of the I-V measurement temperatures, for the MIS diodes with 1, 2 and 4 nm of $TiO₂$. The summary of the results is listed in [Table 1](#page--1-0). As the $TiO₂$ nominal thickness increases, the SBH_{real} decreases and η increases. The diodes with nominal thicknesses of 1 and 2 nm presented η close to unit, especially for higher

Fig. 1. Forward I-V characteristics of Ni/4H-SiC Schottky diodes with 1, 2 and 4 nm of HfO₂ as interfacial layers.

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