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# A comparative study of Hf and Ta incorporations in the dielectric of Pd-$WO_3$-SiC Schottky-diode hydrogen sensor

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ABSTRACT

An investigation on the incorporation of two different kinds of high-κ dielectrics ($HfO_2$ and $Ta_2O_5$) in the dielectric of Pd-$WO_3$-SiC Schottky diode is presented. It is found that while the surface morphology of the $WO_3$ and WHfO films is almost the same, the WTaO film has the smoothest surface due to suppression of oxygen vacancies in $WO_3$ by the Ta incorporation, as supported by XPS analysis. The current-voltage characteristics are examined under a wide range of temperature and hydrogen concentration. Upon exposure to 10,000 ppm $H_2$/air, the diodes based on WHfO and WTaO show a maximum hydrogen response of 89 and 147 respectively, both higher than that (31) of the control sample with $WO_3$. From the kinetics analysis, it is demonstrated that more hydrogen atoms are accumulated at the Pd/WHfO and Pd/WTaO interfaces than their Pd/$WO_3$ counterpart due to larger enthalpy change for hydrogen adsorption on passivated surface, resulting in a greater barrier-height variation at the interface and thus better sensing performance for the two devices with ternary oxide.



## 1. Introduction

As a precious metal, palladium has been studied intensively over the past decades because it plays a significant role in various industries such as jewelry, electronics, dentistry, medicine, groundwater treatment and fuel cell [1],[2]. Hydrogen can easily penetrate and pass through a thin layer of palladium. This implies that under a hydrogen-containing environment, hydrogen adsorbs at not only the palladium surface, but also the "internal" sites located near the metal- substrate interface. Therefore, the properties of the palladium layer and metal-substrate interface could considerably influence the catalytic reactions and hydrogen storage capability under both steady and transient conditions [1].

Researchers have extensively studied the catalytic and reaction kinetics of metal-insulator-semiconductor (MIS) hydrogen sensors based on the Schottky contact of palladium metal due to its high work function (5.1 eV) [2]. In such Schottky-diode-type gas sensors, the adsorption and dissociation of hydrogen change the work function of palladium to modulate the Schottky barrier and thus the current flow through the device. Different types of metal-oxide materials including $SnO_2$, ZnO, $WO_3$ and $MoO_3$ with unique morphological structure have been examined over the past few years [3–6]. Among these, $WO_3$ is recognized as one of the most attractive sensing materials due to its high structural flexibility and stable catalytic behavior [3–6],[7]. This suggests that the oxygen vacancies in $WO_3$ can diffuse from the interior of the material to the surface and vice versa, and the bulk of the oxide has to reach an equilibrium state with the ambient oxygen [8]. Oxygen vacancies are the major point defects that can significantly influence the adsorption process of hydrogen gas. Therefore, to attain good sensing properties for metal oxides, it is necessary to choose materials in which the oxygen diffusion could be suppressed [9]. This work aims to achieve better sensing performance by incorporating two different kinds of high-κ dielectric ($HfO_2$ and $Ta_2O_5$) separately into $WO_3$ as the sensing layer. Hf and Ta are selected as the function element because they are thermally and structurally stable, adjacent to W in the Periodic Table and thus having similar ionic radius as W [12]. Moreover, it has been reported that adding these two elements into other metal oxides such as $La_2O_3$ and $MoO_3$ could improve the electrical characteristics as well as gas sensing performance of the MIS diode [10,11].

## 2. Experimental

Schottky-diode devices were fabricated on n-type 4H-SiC wafer for its benefits of wide bandgap (3.0 eV) and operating capabil-

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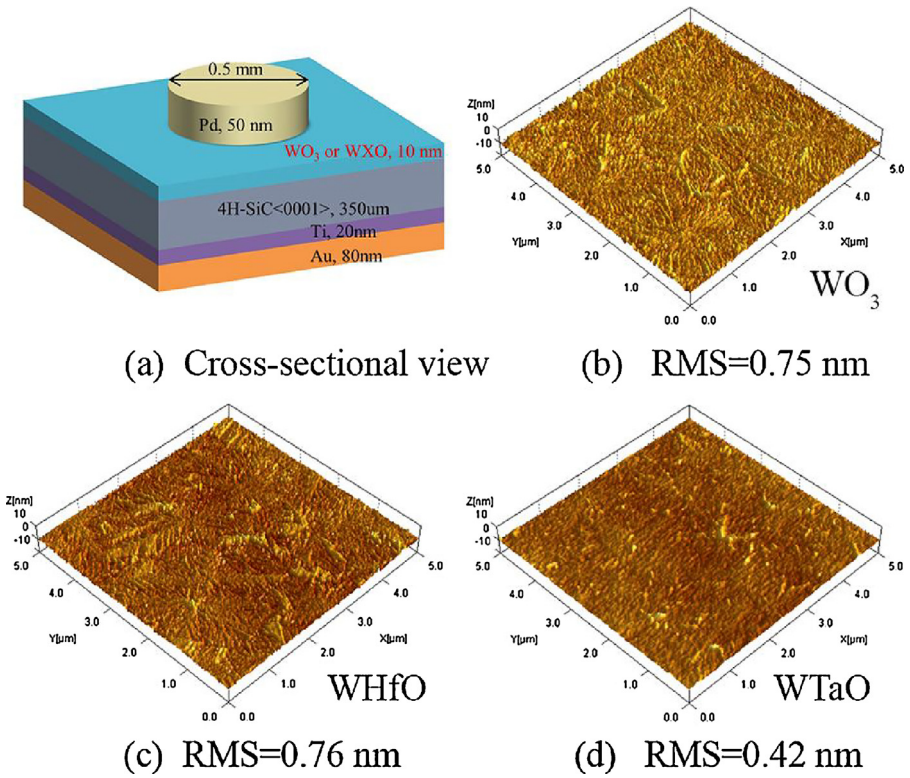


**Fig. 1.** (a) Cross-sectional view of Schottky-diode gas sensor. AFM image with a measurement area of 5 μm × 5 μm: (b) $WO_3$, (c) WHfO, (d) WTaO.

ity in harsh environments. First, a 20 nm-Ti/80nm-Au layer was evaporated on the backside of the cleaned wafers using e-beam evaporation followed by a forming gas (5% $H_2/N_2$) annealing process at 350 °C for 20 min to establish an ohmic contact. Then, a dielectric film, hafnium-tungsten oxide (WHfO, denoted as device B) or tantalum-tungsten oxide (WTaO, denoted as device C), was deposited on the front side of the wafer by reactive co-sputtering method in an $Ar + O_2$ ambient ($Ar:O_2 = 24:1$) with a W-target direct-current (DC) supply of 0.04 A and a $Ta_2O_5$-target or $HfO_2$-target power of 15 W. A pure $WO_3$ film was also prepared as the control sample (denoted as device A). The thickness of all the oxide films was 10 nm as determined by ellipsometry. After sputtering, the samples underwent an annealing in synthetic air at 550 °C for 20 min to achieve a fully–oxidized state for the oxide films. Afterwards, a Pd film with a thickness of 100 nm and an area of 0.2 $mm^2$ was deposited on top of the oxide layers via DC sputtering. Lastly, an annealing process was performed in nitrogen at 350 °C for 20 min to stabilize the Schottky contact.

## 3. Results and discussion

### 3.1. Atomic force microscopy

The cross-section of the devices is illustrated in Fig. 1(a), and the surface morphology of the oxide films was studied by atomic force microscopy (AFM). The root-mean-square (RMS) roughness of the $WO_3$ and WHfO films is almost the same (~0.75 nm), implying that adding $HfO_2$ into $WO_3$ hardly influences its surface morphology. However, the WTaO sample has the smoothest surface with a RMS roughness of 0.42 nm. The reduction in surface roughness should be attributed to the suppression of oxygen vacancy in the dielectric layer by the incorporated Ta, which can serve as a passivating agent [16]. Therefore, less hydroxyl ions form near the Pd/oxide interface and so can improve the hydrogen sensing capability of the device, as confirmed by the results below [12].

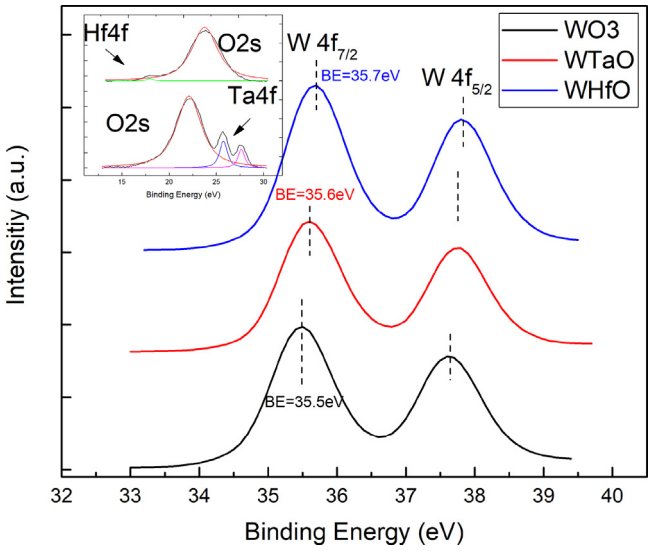


**Fig. 2.** XPS core-level W 4f and O 2s (inset) spectra of the nanostructured oxide films.

### 3.2. X-ray photoelectron spectroscopy (XPS) analysis

The stoichiometric composition of the nanostructured oxide films was analyzed by XPS using Kratos Axis Ultra DLD Spectrometer, and the binding energy of the C 1s peak (284.80 eV) is used as the energy reference for calibration. The inset of Fig. 2 shows the Hf 4f spectrum of the WHfO film and the Ta 4f spectrum of the WTaO film, confirming the effective formation of WHfOx and WTaOx compounds after the annealing. The main graph of Fig. 2 displays the high-resolution core-level W 4f spectra of the three oxide compounds. For the $WO_3$ film, two peaks are observed at binding energy ($E_b$) of 35.5 eV and 37.6 eV, corresponding to W