Extended Abstracts of the 2010 International Conference on Solid State Devices and Materials, Tokyo, 2010, pp685-686

Robust Ultra-violet (UV) Analysis Technique for Band Diagram Extraction of Al/HfGdO/SiO_2/p-Si Structure with Different Hf/Gd Dual-sputtered Ratio

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1. Introduction

State-of-the-art complementary metal-oxide-semiconductor (CMOS) technology requires gate dielectric layers with higher dielectric constant than SiO_2 or SiON as projected in the International Technology Roadmap for Semiconductors (ITRS). Among these high dielectric constant materials, HfO_2 based gate dielectrics are considered as the most promising gate material to match the future ULSI application. Recently, metal-incorporated HfO_2 has drawn great attention such as HfLaO, and HfYO because of the relatively high dielectric constant and low leakage current [1-3]. However, there are only few researches focus on the energy band structure and electron effective mass (m^*) which are significant for material physics. In this study, we chose Gadolinium (Gd) as the incorporated elements in HfO_2 and extracted the physical parameters such as Schottky barrier height (Φ_B), energy band gap (E_g), valence band (E_v), and electron affinity (χ) of HfGdO thin films by a robust ultra-violet (UV) analysis technique.

2. Experiment

Metal–oxide–semiconductor (MOS) capacitor devices with HfGdO gate dielectrics have been fabricated using the following process. First, a thin SiO_2 layer was thermally grown on a p-type (100) silicon substrate as interfacial layer and 5 nm detected by ellipsometer. Subsequently, a 10 nm HfGdO layer was dual-sputtered on the SiO_2 by radio frequency sputtering system in Ar and O_2 ambient at a pressure of 20 mTorr with 3-inch Gd and Hf targets. The schematic of the process and splits are shown in Fig. 1. To survey the dependence between dual-sputtered power ratios (Hf/Gd) and materials, three different power ratios were selected (Hf/Gd=150/0, 150/50, and 150/150). Ultra-violet photoelectron spectroscopy (UPS) and ultra-violet-visible-near infrared (UV-VIS-NIR) were applied to extract the valence band and band gap of HfGdO thin films. For electrical analyses, capacitance-voltage (C-V) and gate leakage current density (J-V) were measured to obtain the oxide trapped charge and electron effective mass by HP 4284 and Angilent 4156C, respectively.

3. Results and Discussion

The bonding energy profile and chemical composition of HfGdO thin films with different Hf/Gd power ratios are illustrated in Fig. 2. It can be found that the chemical composition of each HfGdO thin film is proportional to each power ratio of Hf/Gd. In Fig. 3, metal-silicon work function difference (Φ_{ms}) was extracted as -0.7706 eV by linear fitting the characteristics of flat-band voltage (V_{FB}) versus thickness and the work function of Al metal gate is around 4.1294 eV by using the work function of p-type Si for 4.9 eV. To alleviate the oxide trapped charge in HfGdO gate dielectrics, post deposition annealing (PDA) at 900°C was performed by rapid thermal anneal system (RTA) in nitrogen ambient as shown in Fig. 4. Fig. 5 shows the Hf4f core level and valence-band spectrum for HfGdO films by UPS. The maximum level of valence band for Hf/Gd=150/150 sample can be estimated as 7.1024 eV by the following equation,

$$q\chi+E_g=h\nu-(E_s-E_v) \quad (1)$$

where χ is the electron affinity, $h\nu$ is the incident photon energy, and E_s is the photoemission threshold. E_s and E_v can be interpolated from the linear fits of the onset defined by the electron peak [4]. Parameters of the rest of the power ratios are comprehensively listed in Table 1. The optical transmission spectrum of HfGdO thin films was detected by UV–VIS–NIR as shown in Fig. 6. The E_g can be estimated by assuming a direct band gap between the conduction and valence bands expressed as equation,

$$(\alpha h\nu)^2 = C(h\nu-E_g) \quad (2)$$

where α is the absorption coefficient, and C is a constant [5]. From the $(\alpha h\nu)^2$ versus $h\nu$ curves of HfGdO thin films, it can be observed that with increased Gd elements, the E_g of HfGdO film is also increased. Besides, the $q\chi$ of each sample now can be easily collected by E_v-E_s. To obtain the m^* in the HfGdO film of each dual-sputtered power ratio, Fowler-Nordheim (F-N) tunneling and Schottky emission current measurements are required. Therefore, in Fig. 7, the barrier height of Al/HfGdO (Φ_B) was extracted by linear fitting of the gate leakage current at F-N tunneling region. Meanwhile, Schottky emission characteristics with elevated temperature was fitted until the dynamic dielectric constant is equal to the square of the index of refraction and shown in Fig. 8. According to Fig. 7 and Fig. 8, the electron effective mass (m^*) and Φ_B of Al/HfGdO barrier can be calculated with self-consistent iteration method as exhibited in Fig. 9 [6]. Subsequently, the energy band diagram of the Al/HfGdO/SiO_2/p-Si structure can be successfully obtained and shown in Fig. 10. Specific physical parameters of band diagram are organized in Table 1.

4. Conclusion

In this study, we obtain the energy band diagram of Al/HfGdO/SiO_2/p-Si structure by integrating the robust U-V analysis technique and electrical measurements. The valence band (E_v) and energy band gap (E_g) of the HfGdO gate dielectrics were extracted by using the UPS and UV–VIS–NIR analysis systems respectively. In addition, the Al/HfGdO barrier height and electron effective mass were successfully obtained by self-consistent iteration method. The analysis technique is believed to be important for future material physics.

Acknowledgement

This work was supported by the National Science Council under the contract of NSC 98-2221-E-182-057-MY3 and NSC98-2218-E-182-002-MY2.

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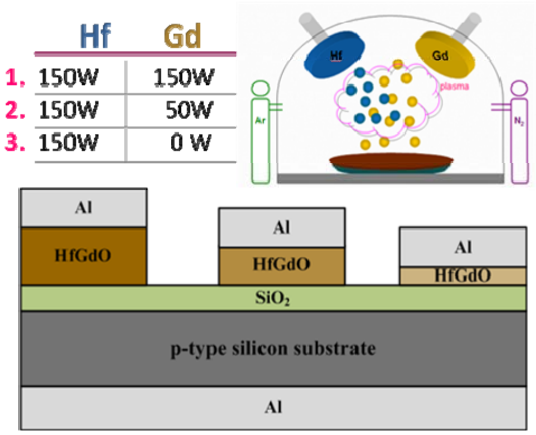

Fig. 1 Schematic of dual-sputtered method and process splits. Three different power ratios were performed to understand the dependence between incorporated Gd amount and material characteristics.

Table 1 Physical parameters of E_s, E_v, E_g, χ, Φ_B, and m^* for $Al/HfGdO/SiO_2$/p-Si structure with various dual-sputtered power ratio.

Hf/Gd	150/0	150/50	150/150
Es	11.913 eV	12.8845 eV	13.1662 eV
Ev	7.8878 eV	7.3856 eV	7.1024 eV
Eg	5.4433 eV	5.802 eV	5.8485 eV
χ	2.4445 eV	1.5836 eV	1.2539 eV
ΦB	1.5928 eV	2.059 eV	1.776 eV
m*	0.572 m0	0.2206 m0	0.768 m0

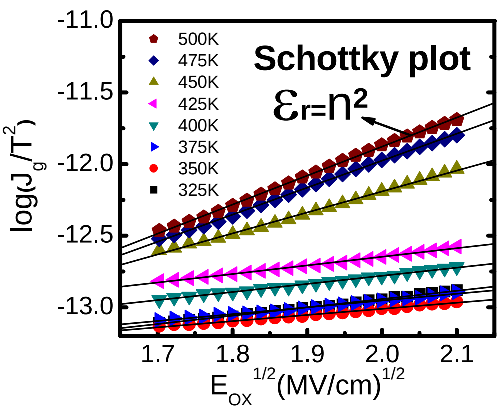

Fig. 8 Schottky emission fitting with elevated temperature of $Al/HfGdO/SiO_2$/p-Si structure. Dynamic dielectric constant is equal to the square of the index of refraction at 500K.

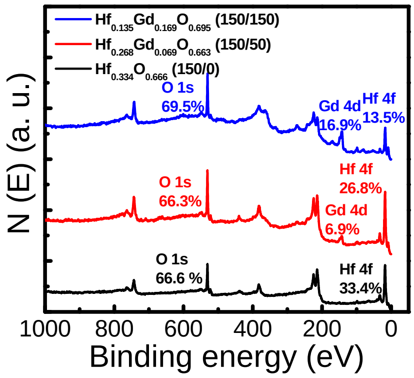

Fig. 2 Binding energy and chemical composition of 10 nm HfGdO films with various dual-sputtered power ratio.

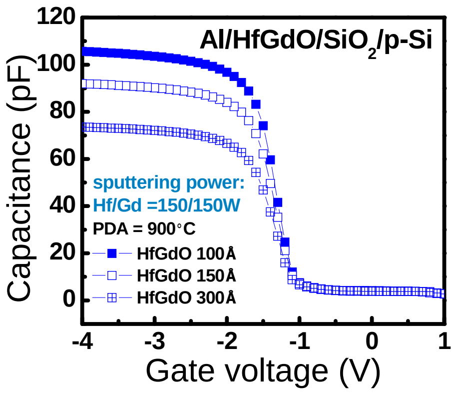

Fig. 4 C-V curves of $Al/HfGdO/SiO_2$/p-Si structure with 150/150 dual-sputtered power ratio and different HfGdO thickness.

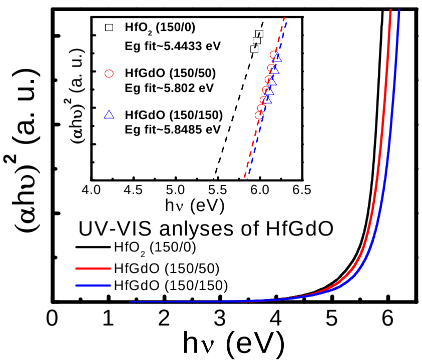

Fig. 6 The optical transmission spectrum of HfGdO thin film by UV–VIS–IR and the fitting of $(\alpha h\nu)^2$ versus $h\nu$ curves for HfGdO thin films was shown in inset.

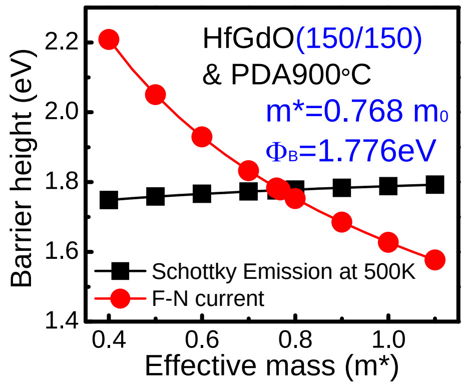

Fig. 9 Electron effective mass (m^*) and barrier height fitting of $Al/HfGdO/SiO_2$/p-Si structure and m^* is calculated as 0.768 m_0 and Φ_B is 1.776 eV.

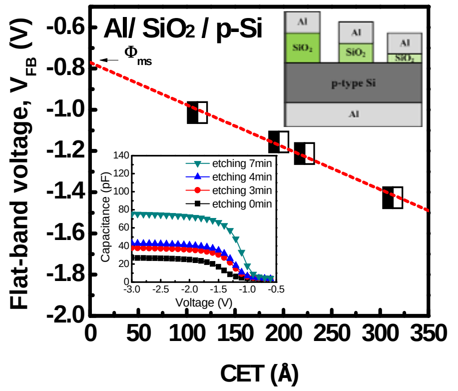

Fig. 3 A1 metal gate to silicon work function difference (Φ_{ms}) extraction of Al/SiO_2/p-Si structure.

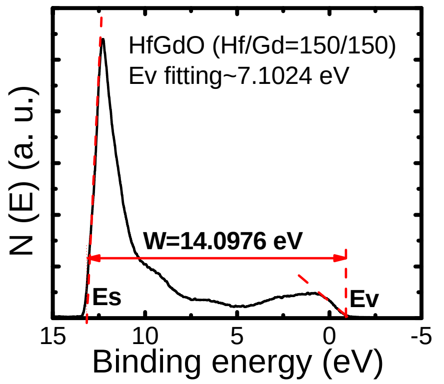

Fig. 5 Hf4f core level and valence-band spectrum for HfGdO film. The corresponding valence-band edge is about 7.1024 eV.

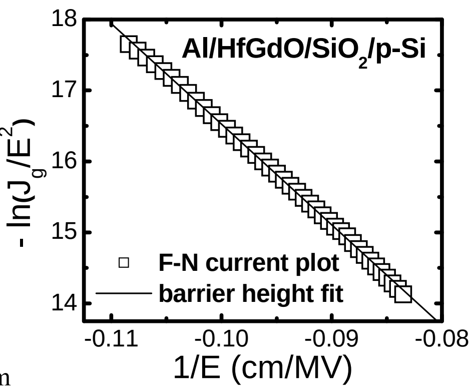

Fig. 7 F-N tunneling fitting plot of $Al/HfGdO/SiO_2$/p-Si structure to extract the Al/HfGdO barrier height (Φ_B).

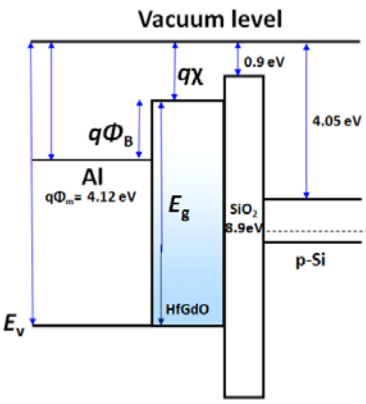

Fig. 10 Energy band diagram of $Al/HfGdO/SiO_2$/p-Si structure. Detailed parameters are listed in Table 1.