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Effect of Annealing on Pyroelectric Response and Aging Behavior of Al-doped HfO_2 Thin-films

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Summary:

Doping and annealing have been effective in improving the pyroelectric properties of hafnium oxide thin films (HfO_2). A blind spot is the effect of these on their durability. To unravel this, we characterized the temporal decay (in terms of pyroelectric response) of 10 nm thick Al-doped HfO_2 films (HAO) that are annealed at 650°C and 800°C. Remarkably high pyroelectric coefficient of about 91.5 $\mu C/m^2 \cdot K$ was repeatedly detected in HAO films annealed at 800°C. Unlike existing Zr-/Si-doped HfO_2 films (HZO and HSO), the HAO films exhibit unique aging behaviors that are characterized by significantly lower decay rates, making it a promising material for precision sensing and thermal energy harvesting.

Keywords: aging behavior, doping, hafnium-dioxide, nanoelectronics, pyroelectrics, thin-films

Background, Motivation and Objective

The performance of pyroelectrics is usually evaluated based on remnant polarization and pyroelectric coefficients. Doping and annealing have been applied to optimize these properties [1]. For hafnium oxide (HfO_2) thin films [2], elements such as Zr, Al, Si etc. have been used as dopants to stabilize the orthorhombic crystal phase of the material [1,3,4]. However, these metrics alone do not conclude their long-term durability, as factors such as noise and aging could undermine their performance in the device [5]. Consequently, pyroelectric sensors could have poor sensitivity and be imprecise, while pyroelectric energy harvesters could exhibit noisy AC-to-DC conversion. Therefore, it is important to understand the aging behavior of pyroelectrics of different chemical compositions and thermal treatment. To this end, this paper examines the temporal decay of pyroelectric response of 10 nm thick Al-doped HfO_2 thin films (HAO) annealed at 650°C and 800°C, using Zr-doped HfO_2 (HZO) and Si-doped HfO_2 (HSO) as reference samples.

Materials and Methods

First, the HAO firms were prepared by thermally enhanced atomic layer deposition (ALD), using hafnium-tetrachloride ($HfCl_4$), water (H_2O), and trimethylaluminum (TMA) as precursors, as shown in Fig. 1. Similar processes were used to deposit the HZO and HSO films. The electrical characterization setup is shown in Fig. 2, it comprises a Peltier's element for sinusoidal heating, a Pt-100 temperature sensor and a picometer that detects the pyroelectric current via a probe needle.

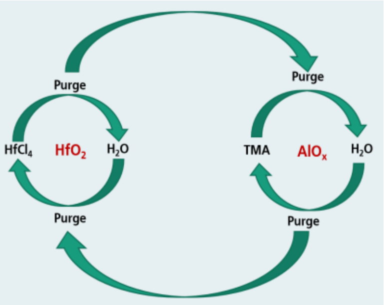

Fig. 1. Schematic of ALD doping cycles for HAO.

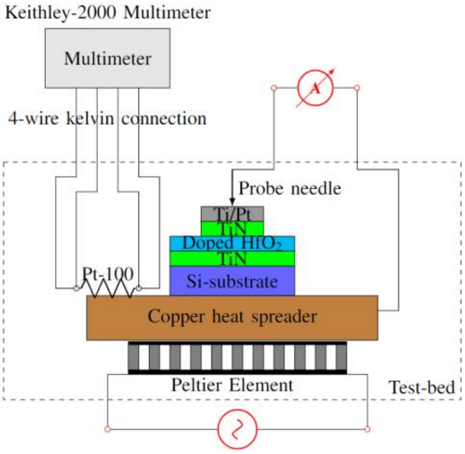

Fig. 2. Schematic of Pyroelectric probe setup.

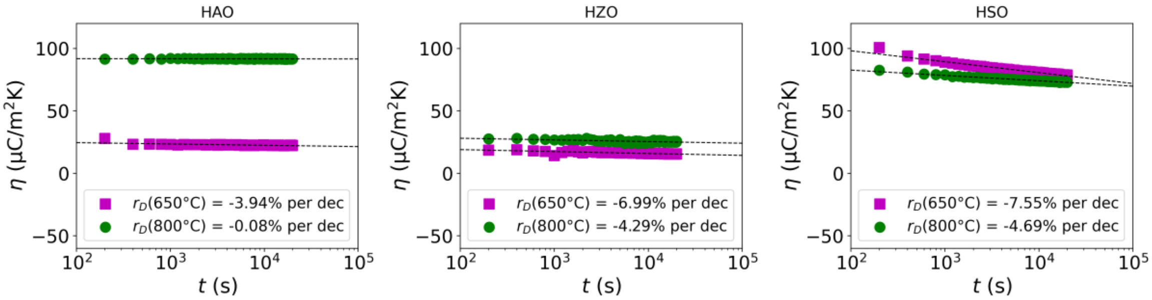

Fig. 3. Plots comparing the aging of HAO with HZO and HSO films (η: Pyroelectric coefficient, r_D: Decay rate).

Using this system, the temporal decay of the films are determined by rapid measurement of pyroelectric coefficient for 200 s and in 100 super cycles. By fitting with exponential decay function, the decay rates (r_D) of the samples are extracted.

Results

The experimental results, presented in Fig. 3 and Fig. 4, show that the HAO film annealed at 800°C exhibits sufficiently high pyroelectric coefficient of about 91.5 μC/m²·K and a significantly lower decay rate of -0.08% per decade compared to the HZO and HSO samples annealed at the same temperature, which aged at the rate of -4.29% and -4.69% per decade, respectively. A similar trend is observed for samples annealed at 650°C.

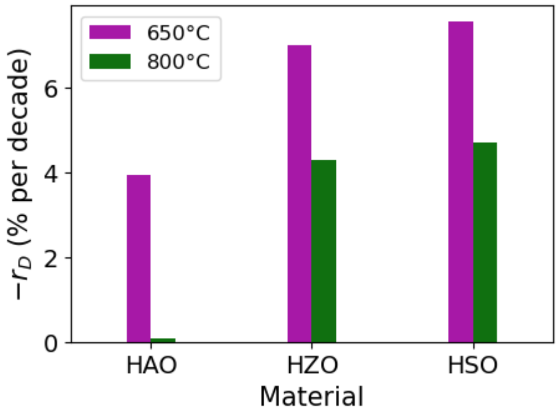

Fig. 4. Bar plot of pyroelectric decay rates.

Conclusion

Our study provides novel insights on the pyroelectric property of hafnium oxide films. Notably, HAO samples that are annealed at 800°C stand out with the most desirable pyroelectric responses, which are characterized by high pyroelectric coefficients that range within those of the HSO samples. Also, its decay rates are much lower than those of the HAO annealed at 650°C, HZO and HSO samples. Therefore, this HAO material can be used to develop precision infrared sensors and efficient thermal-to-electric energy transducers for various applications.

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