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Intriguing conducting properties of HfO_xN_y thin films prepared from the $Hf[N(C_2H_5)_2]_4$

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Hafnium nitride films were prepared on the Si(100) substrates by the metal-organic chemical vapor deposition method using $Hf[N(C_2H_5)_2]_4$. The prepared samples were then oxidized in air, followed by rapid-thermal annealing to produce HfO_xN_y thin films, meanwhile the associated physical properties were investigated. The x-ray photoelectron spectroscope analysis unveiled that the composition of the films is HfO_xN_y. In addition, the films after the rapid-thermal annealing treatments at various temperatures revealed salient features in their physical properties, such as capacitance and conductivity. On this basis, the feasibility of using the HfO_xN_y layers as high-*k* dielectrics in complementary metal oxide semiconductor transistors was also discussed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2405848]

Thin film hafnium oxide has long been recognized as a potential high dielectric material owing to its relatively high dielectric constant, wide band gap (5.68 eV), and compatibility with polysilicon gate electrodes.[1–3] However, the oxide thin film readily crystallizes, resulting in a marginally high leakage current.[4] Moreover, it is liable to form a $HfSiO_x$ interlayer towards the Si top electrode.[5,6] Through strategic design and synthesis, several modifications of hafnium-based dielectrics have been performed to avert these shortcomings. The elements Si, Al, and N have been injected into the oxide layer to form HfSiO,[7] HfAlO,[8] HfON,[9–11] and HfSiON.[12] Among the various modifications, prohibiting crystallization of HfO_2 with addition of Al or Si is considered inferior because the dielectric constant decreases upon increase in the dopant concentration. Alternatively, nitrogen is preferable mainly due to its abundance, stability, and versatility. Herein, we report the growth and characterization of HfO_xN_y thin films and compare their electrical and other physical properties to those of HfO_2 films for high-*k* applications.

Based on chemical concepts, a simple straightforward growth method, a pulsed liquid-injection metal-organic chemical vapor deposition (MOCVD) technique,[13] was implemented to form N-containing Hf films. $Hf[N(C_2H_5)_2]_4$,[14,15] tetrakisdiethylamidohafnium (TDETH, ATMI Co.), evaporated at 450 K with a pulsed (1–3 Hz) Ar gas stream [100 SCCM (SCCM denotes cubic centimeter per minute at STP)] was used as the precursor. Hafnium nitride thin films were deposited on *p*-type Si(100) substrates at 773 K and annealed for 5 min *in situ*. Then oxidation of those films was executed at 300±1 K with humidity of 45%±5% for 4 h. Finally, the thin films were rapid thermal annealed (RTA) at 773–1223 K for 2 min under a nitrogen atmosphere. This sequence of procedures provided a stable oxidized film with poor crystallinity.

Figure 1(a) depicts the x-ray photoelectron spectroscopy (XPS) fitting data of Hf 4*f* of HfO_xN_y thin films deposited on *p*-type Si substrates. Two segments located at 15.3 and 17.1 eV are assigned to Hf–N and Hf–O bindings, respectively. All spectra in Fig. 1(b) are normalized so that their intensities are the same as that of Hf $4f_{7/2}$ at 15.3 eV. As the temperature of RTA increases, intensities of the electrons of Hf–O bonding, at 17.1 eV for Hf (not shown here) and at 531.4 eV for O [see Fig. 1(b)], decrease together. Meanwhile, the N intensity keeps the same as the RTA temperature is increased from 873 to 1223 K under nitrogen. The result

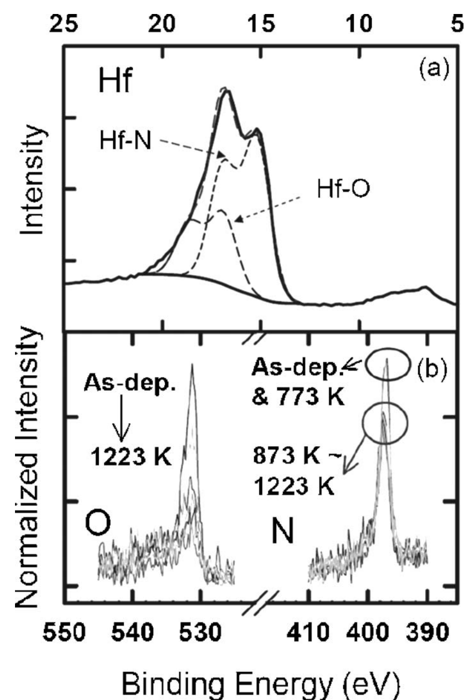

FIG. 1. XPS spectra of HfO_xN_y films prepared at RTA temperatures of 773–1223 K. (a) Hf 4*f* electrons. (b) N and O 2*p* electrons.

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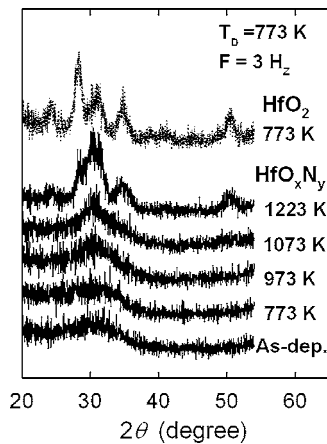

FIG. 2. Glancing angle XRD patterns of HfO_xN_y and HfO_2 thin films prepared via RTA at 773–1223 K.

clearly indicates that oxidation of the films by RTA under a nitrogen atmosphere was not efficient at higher temperatures because escaping of dangling O was enhanced.

Field emission scanning electron microscope images (not shown here) of the films annealed at various temperatures indicate that the particle size increases with increasing annealing temperature. X-ray diffraction (XRD) data shown in Fig. 2 also suggest that the crystallinity increases as the RTA temperature is raised. The parallel increases of inhomogeneous size distribution and degree of crystallization suggest that mobility and degrees of freedom of the surface particles increased during nucleation at high temperatures. For a fair comparison, an XRD pattern of the HfO_2 thin film prepared via RTA at 773 K is also shown at the top of Fig. 2. Obviously, the HfO_2 sample reveals a more resolved pattern, while the HfO_xN_y films are much less ordered. More importantly, the degree of crystallization, as supported by the structureless patterns at low temperatures, decreases with lowered RTA temperatures. The results clearly demonstrate that incorporation of both N and O atoms into the films greatly impairs the crystallization process, in which RTA temperature also plays a crucial role. How this affects the electrical properties of the films is discussed below.

MOS capacitors with HfO_xN_y dielectrics prepared at different RTA temperatures were fabricated. Thickness of the as deposited, the RTA processed at 773 K, and the one annealed at 1223 K was determined with an N&K analyzer to be 116, 102, and 51 nm, respectively. Typical *C-V* and *I-V* curves of the devices, without any hysteresis, are shown in Fig. 3.

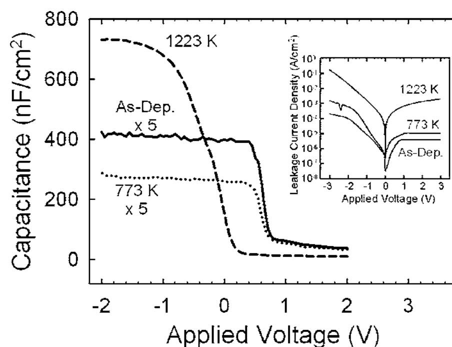

FIG. 3. *C-V* characteristics of HfO_xN_y thin films, as deposited (—), RTA at 773 K (···), and RTA at 1 223 K (---). Inset: *I-V* characteristics of samples processed at different RTA temperatures.

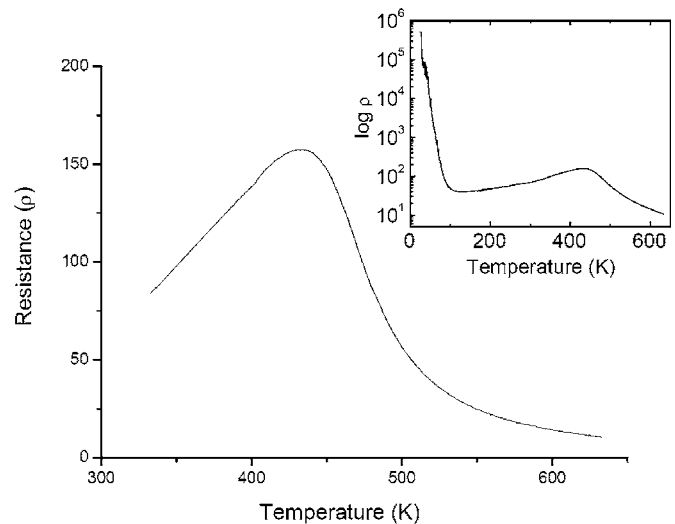

FIG. 4. Plot of resistance vs temperature measured under 4.0 Pa for a HfO_xN_y thin film rapidly annealed at 973 K. Inset: The logarithmic data from 40 to 630 K.

Capacitance of the layer annealed at 1223 K reveals the lowest flatband voltage at $V_{fb}=0.2$ V while both of the as-deposited and the 773 K annealed samples display the voltages at 0.7 V. The result is similar to that observed in silicon oxynitride devices[16] and can thus be rationalized by formation of localized positive charges at high annealing temperatures. It should be noted that a low leakage current is observed for the as-deposited thin film while variable leakage values are seen for the annealed samples. The samples annealed at 873–1073 K were metallic as shown in a resistant versus annealing temperature plot (not displayed here). These samples are ignored for the dielectric value estimation. The *k* values are measured to be 9 and 42 for the samples annealed at 773 and 1223 K, respectively. In addition to other factors, a significant thickness shrinking at 1223 K may contribute to the increased *k* value. For comparison, the *k* value of HfO_2 is 25.[3]

Another salient feature is the electric conductivity, which, measured with a four-point probe, was distributed from a range of conductorlike to insulation (not shown here). The leakage current of thin films annealed at 873–1123 K exhibits mixed behavior of conductorlike and semiconductor properties, while the films prepared at as deposited, 773 and 1223 K, are insulatorlike. To gain detailed insight into the associated electrical properties, the metal-like behavior film prepared at 973 K via RTA was selected to gauge the changes of resistance as a function of temperature. Figure 4 depicts a plot of resistance (R) versus temperatures (T) for a HfO_xN_y thin film prepared via RTA at 973 K. Of particular interest is the appearance of a rise and a decay component in the temperature range of 310–630 K. The rise component appears to be linear at 310–430 K and can be well fitted by $R\sim-190+0.82T$, indicating a conductorlike property, while the decay follows first order exponential behavior and can be fitted with $R=5+0.0016e^{-5200/T}$, a typical property of the semiconductor. The interplay between these two properties gives rise to a peak temperature at 430 K. The reproducibility and reversibility of the results eliminate any artifacts caused by the instrumentation. In addition, purging N_2 during *R-T* measurement has negligible effect on the *R-T* plot. Accordingly, the oxidation reaction, due to trace amount of

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oxygen existing in the vacuum system, can also be discarded. Thus, the peak around 430 K may originate from either phase transition or a subtle temperature-dependent variation of the films. The former case is very unlikely since the phase transition temperature is expected to be well above 340 K for the HfO_xN_y film. In fact, that HfO_xN_y is not a stochiometric compound, to a certain extent, and can have local variations in O and N contents, despite the global homogeneous measured experimentally. Thus it is possible have conductive fine lines embedded in a semiconductor matrices. Assuming that the density of the conductive lines is greater than the percolation threshold, then the conductivity of the sample is a sum of both as shown below:

$$\sigma = \sigma_{\text{metal}} + \sigma_{\text{semi}}. \quad (1)$$

Evidently, σ_{metal} is proportional to $1/T$ and σ_{semi} is proportional to $e^{-T_0/T}$ according to simple Drude model.[17] It is also noticeable that, as supported by the steep slope of the plot within 310 and 430 K, most areas of the films are believed to be semiconductorlike.

As the temperature was decreased to below room temperature, the plot of R vs T remains a linear behavior down to 150 K, followed by a rapid rising with an R/T relationship of $R \sim 265e^{(50/T)^4}$ (see inset of Fig. 4). The results can be tentatively rationalized by a mechanism incorporating electron trapping. Due to the inhomogeneous distribution of composition, there exist certain defects among the conducting fine lines to trap electrons. As temperature is low enough (i.e., <150 K) that trapped electrons have insufficient thermal energy to escape, and the resulting conductivity is accordingly reduced drastically. Furthermore, one cannot eliminate the possibility of the occurrence of certain local phase transitions at ~ 150 K, which may also play a role in impeding the conductivity. Work focusing on this is currently in progress and the results will be published in a separate issue.

In conclusion, we report the intriguing, previously unrecognized physical properties of the high dielectric material, HfO_xN_y, prepared from a single precursor $Hf[N(C_2H_5)_2]_4$, via MOCVD followed by controlled oxidation and RTA steps. Despite HfO_2 thin films being the most noticeable material in the preparation of the high dielectric films, HfO_xN_y prepared via the steps described in this study may furnish a potential material because of its strong inhibition to crystallization as well as the great enhancement in capacitance.[18] Furthermore, in potential high-k device applications, the advantage of HfO_xN_y over HfO_2 lies in its physically greater thickness under the same equivalent oxide thickness. We thus believe that the prepared films may provide a stable interface layer with a high dielectric constant. This, in combination with the intriguing physical properties elaborated above, may spark a broad spectrum of interest in view of possible applications.

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