# Electronic Structure of $HfO_xN_y$ Thin Films Fabricated by Ion-Assisted Reactive Sputtering Deposition

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**Abstract – $HfiO_xN_y$ films have been fabricated at Si substrates by reactive ion assisted sputtering deposition. Chemical composition of the films was determined with X-ray photoelectron spectroscopy (XPS). Optical parameters of the films were defined with spectroscopic ellipsometry (SE).**

## 1. Introduction

$HfO_2$ and $HfO_xN_y$ films are actively developed as high-*k* dielectrics for new generation of metal-oxide-semiconductor (MOS) structure [1–3]. Besides this, hafnium oxynitrides possess pronounced photocatalytic reactivity under sunlight illumination. Nitrogen-doped hafnium oxide films show good interface properties with Si substrates and can be readily fabricated by sputtering deposition in $N_2/O_2$ reactive gas mixture [4, 5]. This study is aimed to fabricate the $HfO_xN_y$ films with reactive sputtering deposition method and define the electronic properties with X-ray photoemission spectroscopy (XPS) and spectroscopic ellipsometry (SE).

## 2. Experiment

The $HfO_xN_y$ films were grown using ion beam sputtering of Hf metal target. The reactive gas mixture $N_2/O_2$ ratio was taken as 100/0, 80/20, and 0/100.

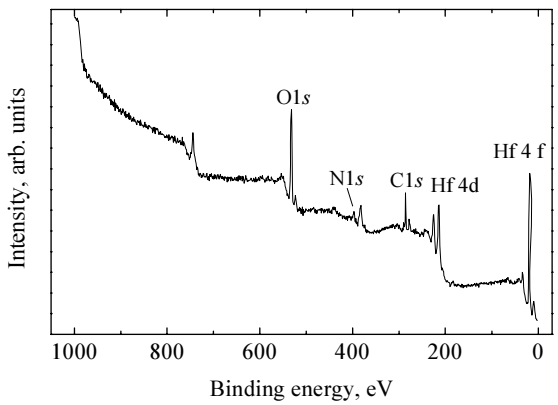


Fig. 1. Survey photoemission spectrum recorded for sample 3 fabricated at $N_2/O_2$ = 100/0

Survey photoemission spectrum showed presence of hafnium, carbon, nitrogen and oxygen (Fig. 1).

Oxygen presence in the film was detected for all the three samples. Two different chemical states of nitrogen and two different chemical states of hafnium were detected in the films made under $N_2/O_2$ = 100/0 and 80/20 reactive gas partial pressure. Binding energy splitting measured for Hf 4f components was as high as ~1 eV (Fig. 2).

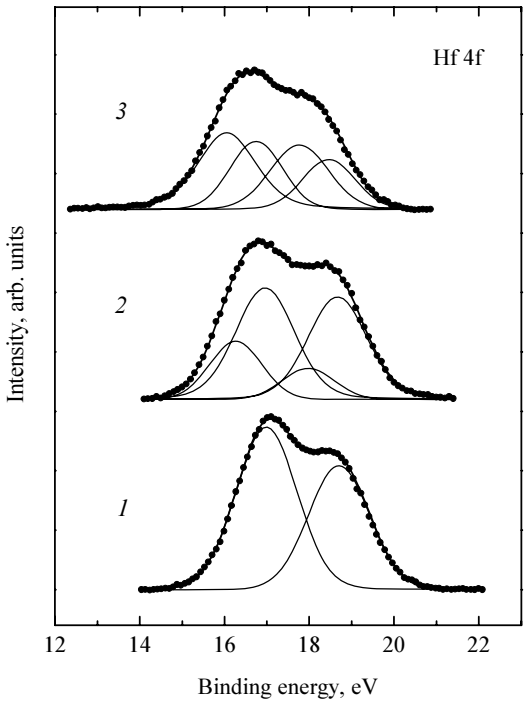


Fig. 2. Detailed photoemission spectra of Hf 4f doublet. Samples are given by numbers

Giant binding energy difference ~4.7 eV was observed for N 1 s core level components. Optical characteristics and film thickness were evaluated with SE over the spectral range 250–800 nm (Table 1).

No optical absorption was detected for the films fabricated at $N_2/O_2$ = 100/0, 0/100. An absorption band at $\lambda$ = 300 nm has been found for the film synthesized

Table I. Synthesis conditions and composition of $HfO_xN_y$ films

| Sample number | 1 | 2 | 3 |
|---|---|---|---|
| Gas composition $N_2/O_2$, % | 0/100 | 96/4 | 100/0 |
| Thickness, nm | 83.1 | 67.3 | 71.1 |
| Surface chemical composition by XPS, % at. | | | |
| Hf | 26.57 | 24.66 | 24.83 |
| C | 16.96 | 17.94 | 18.14 |
| N | – | 3.60 | 5.98 |
| O | 56.47 | 53.80 | 51.05 |

at $N_2/O_2$ = 80/20 that is an indicator of noticeable decrease of the forbidden energy band gap in this case. Photocatalytic activity of $HfO_xN_y$ films was measured by acetone oxidation reaction in the homemade setup. The test for complete acetone oxidation by nitrogen-doped films shows the photocatalytic reactivity ~0.25 nmol/c.

## References


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