Effect of N₂O gas for Reactive Sputtering Deposition of ($\lambda/4$) HfO₂ / ($\lambda/4$) SiO₂ Distributed Bragg Reflector

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This paper demonstrates the effect of N₂O gas on HfO₂ thin film and ($\lambda/4$) HfO₂ / ($\lambda/4$) SiO₂ distributed Bragg reflector (DBR) during reactive sputter deposition. HfO₂ thin film fabricated with N₂O as reactive gas during sputter deposition improved its surface roughness and crystal structure. A remarkable improvement of optical transmittance in HfO₂ thin film deposited with N₂O gas was also found. An optimum supply of oxygen atoms is considered to give efficient oxidation for hafnium metal during reactive sputter deposition due to the relatively small dissociation energy from N₂O molecules to N₂ molecules and O atom. The transmittance of ($\lambda/4$) HfO₂ / ($\lambda/4$) SiO₂ DBR value was obtained to be 98 %. This value is close to the optical transmittance of the dielectric multilayer for highly efficient microcavity.

Key words: HfO₂ thin film, Optical transmittance, N₂O gas, Sputter deposition

1. INTRODUCTION

In recent years, the optical microcavity has received much attention as a means to improve a semiconductor laser diode, because it has advantageous features of low lasing threshold, single mode oscillation and low output beam divergence angles. The vertical microcavity is composed of an active layer sandwiched by distributed Bragg reflectors (DBRs) as shown in Fig. 1. In this cavity, the specific wavelength (λ) light is confined in the active layer due to the optical stop band, and high photon density occurs in the active layer, which bring about the enhancement of the spontaneous and stimulated emissions, and lead to the low lasing threshold.

The DBR is composed of a multilayer of high dielectric layer and a low dielectric layer. Table I shows the dielectric constant and transparent region at the short wavelength side (< 400 nm) in the candidate materials of DBR for short wavelength. High optical transmittance (> 99 %) of the dielectric layers of DBR is required for highly efficient microcavity. However, many high dielectric materials are not transparent at the short wavelength side due to the optical inter band transitions. As shown in Table 1, it is found that HfO₂ material is one of the candidate materials of high dielectric layer for the short wavelength DBR.

We have fabricated ($\lambda/4$) HfO₂ / ($\lambda/4$) SiO₂ DBR by a magnetron sputter deposition using Ar gas so far.[1] Here the specific wavelength (λ) was set to be 400 nm. SiO₂ thin film with low dielectric constant and wide band gap showed the high optical transmittance of 99 % at 250 nm (5.0 eV) – 600 nm (2.0 eV). On the other hand, HfO₂ thin film with the high dielectric constant and the lower band gap showed the low optical transmittance of 70 % at short wavelength region

Fig.1 Schematic illustrations of a vertical microcavity (left) and a simulated optical transmittance spectrum of DBR (right).

Table I Dielectric constant and transparent region at short wavelength side (< 400 nm) in the candidate materials of DBR

Material	Dielectric Constant	Transparent Region
TiO ₂	86 (E ⊥ c) ²⁾	> 400 nm (×)
HfO ₂	23 ³⁾	> 220 nm (○)
ZrO ₂	22 ⁴⁾	> 340 nm (×)
Y ₂ O ₃	11.8 ²⁾	> 300 nm (×)
Al ₂ O ₃	9.5 ²⁾	> 200 nm (○)
SiO ₂	3.8 ²⁾	> 150 nm (○)

Fig. 2 AFM images of HfO_2 thin films fabricated with Ar gas (a), $Ar+O_2$ gas (b) and $Ar+N_2O$ gas (c) during the sputter deposition, respectively. Here the flow rate of O_2 or N_2O is 1.5 sccm.

of 250 nm (5.0 eV) – 350 nm (4.0 eV). In another study, HfO_2 thin film easily creates oxygen vacancies and defects during sputter deposition, which leads to an optical loss at around 4 eV [5].

In order to supply oxygen efficiently into the thin film, we focused on N_2O gas, because the dissociation energy from N_2O molecules into N_2 molecules and O atom, which is 167 kJ/mol, is about 1/3 of that of from O_2 gas into two O atoms, which is 498 kJ/mol. In this study, the effect of N_2O gas was investigated for HfO_2 thin film and $(\lambda/4)$ HfO_2 / $(\lambda/4)$ SiO_2 DBR during reactive sputtering deposition.

2. EXPERIMENTAL PROCEDURES

HfO_2 thin films with thickness of 200 nm (λ) and $(\lambda/4)$ HfO_2 / $(\lambda/4)$ SiO_2 DBR were fabricated on SiO_2 glass substrates by an RF magnetron sputtering method. The RF power was set to be 100 W, while target-substrate distance was 60 mm. The base pressure was 10^{-5} Pa. Ar gas was introduced as sputtering gas. And N_2O or O_2 gas was introduced as reactive gas. The Ar gas flow rate was set to be 7.8 sccm (2.0×10^{-1} Pa), and N_2O or O_2 gas flow rate was changed from 0 to 2.0 sccm.

The surface morphology of the sample was evaluated by an atomic force micrograph (AFM), and the crystal structure was analyzed by an X-ray diffraction (XRD) measurement. Optical property was evaluated by an optical transmittance measurement.

3. RESULTS and DISCUSSIONS

3.1 Surface morphology and crystal structure

Fig. 2 shows the AFM images of HfO_2 thin films fabricated with Ar gas, $Ar+O_2$ gas and $Ar+N_2O$ gas during the sputter deposition, respectively. In here, O_2 or N_2O gas flow rate is 1.5 sccm. In the AFM image of Ar gas sample, many holes are observed on the surface and the grains do not appear. And its surface is rough compared to another two samples, that value of R_a is obtained to be 5.48 nm, in here with 10 μm measurement scale. On the other hand, the

surfaces of $Ar+O_2$ and $Ar+N_2O$ samples are dense and smooth. The surface roughness of these two samples are almost the same, whose values of R_a are 3.81 nm for $Ar+O_2$ sample and 3.52 nm for $Ar+N_2O$ sample, respectively. And the grains are observed on the surfaces of these two samples. As shown in Figure 2, the grain size of 177 nm in $Ar+N_2O$ sample is larger than that of 118 nm in $Ar+O_2$ sample.

Fig. 3 shows XRD patterns for HfO_2 thin films with various process gas samples. The broad and weak XRD peak appear at around 30° in Ar gas sample. This HfO_2 thin film is considered to be almost amorphous. On the other hand, the diffraction peak of the HfO_2 crystal is observed at around 28° in the thin films deposited with reactive gas. Thus, $Ar+O_2$ and $Ar+N_2O$ samples are considered to be partially crystallized. The intensity of XRD peak for $Ar+N_2O$ sample is higher than that of $Ar+O_2$ sample. The HfO_2 thin film deposited with N_2O gas is considered to much more crystallized compared to the sample

Fig. 3 XRD patterns of HfO_2 thin films fabricated with Ar gas (a), $Ar+O_2$ gas (b) and $Ar+N_2O$ gas (c) during the sputter deposition, respectively.

deposited with O_2 gas due to the efficient supply of oxygen into the thin film during sputter deposition.

3.2 Optical Transmittance for HfO_2 thin films

Fig. 4 shows optical transmittance spectra of the HfO_2 thin films fabricated with various process gases under the same flow rate condition of 1.5 sccm. In here, the wave undulation of each spectrum is due to light interference. Therefore the maximum values of optical transmittance spectra are compared in the following discussion. The value of transmittance of HfO_2 thin film with the reactive gas of O_2 or N_2O is about 90 % at around 4.0 eV, and it appears larger than 95 % at around 3.0 eV. These values are higher than those of 60 % at around 4.0 eV and 85 % at around 3.0 eV of the film without the reactive gas. Thus the transmittance of the thin films deposited with the reactive gas of N_2O or O_2 is found to be much improved, compared to that without the reactive

Fig. 4 Optical transmittance spectra of HfO_2 thin films supplied with Ar gas (---), $Ar+O_2$ gas (- · -) and $Ar+N_2O$ gas (—) during the sputter deposition, respectively.

Table II Optical transmittance at around 3.0 eV for HfO_2 thin films fabricated with $Ar+O_2$ gas or $Ar+N_2O$ gas under the flow rates of 1.0, 1.5 and 2.0 sccm.

	$Ar+N_2O$	$Ar+O_2$
Flow rate (sccm)	Transmittance (%)	Transmittance (%)
1.0	95.4	91.6
1.5	98.1	94.5
2.0	94.1	94.2

gas.

The difference of transmittance values between $Ar+N_2O$ sample and $Ar+O_2$ sample are compared at around the specific wavelength of 3.0 eV (~ 400 nm) of the DBR. Under the same flow rate condition of 1.5 sccm, the transmittance value of $Ar+N_2O$ sample, which is 98 %, is higher than that of $Ar+O_2$, which is 94.5 %.

Table II shows summarized data of optical transmittance at around 3.0 eV for HfO_2 thin films fabricated with $Ar+O_2$ gas or $Ar+N_2O$ gas under the flow rates of 1.0, 1.5 and 2.0 sccm. The transmittance values of the $Ar+N_2O$ samples are higher than those of the $Ar+O_2$ samples under the flow rates of 1.0 sccm and 1.5 sccm. The transmittance of the HfO_2 thin film is improved by utilizing the N_2O gas as the reactive gas.

Generally, an optical transmittance property of a film is affected by contained impurities, vacancies and dislocations in the film, and the surface roughness. The optical loss due to the surface roughness is considered to be negligible in all the deposited HfO_2 films, because its value of R_a , which is about 5 nm maximum, is small, i.e., R_a – the measurement scale ratio is 5×10^{-4} .

In deposited HfO_2 thin film fabricated with Ar gas, the optical loss is considered to be caused by the many oxygen vacancies and defects in the film due to the lack of oxygen atoms during the film deposition. In fact, many holes are grown on the surface. On the other hand it is considered that reduction of vacancies and defects due to supply of oxygen atoms during the sputter deposition gives higher optical transmittance in the samples fabricated with reactive gas N_2O or O_2 . In $Ar+N_2O$ sample, an optimum supply of oxygen atoms is considered to be done during the sputter deposition. This is because the dissociation energy from N_2O molecules into N_2 molecules and O atom is smaller than that of from O_2 gas into two O atoms, resulting in the efficient oxidation for hafnium metal during reactive sputter deposition occurs.

It is possible that the grain boundaries cause optical loss of the film. In $Ar+O_2$ and $Ar+N_2O$ samples, HfO_2 thin films are crystallized and the grains are formed. However, the grain size of each sample is smaller than 200 nm, the value of which is compared with the specific wavelength ($\lambda = 400$ nm). Moreover the grains are dense in these deposited HfO_2 thin film introduced the reactive gas. Therefore the influence of grain boundaries to optical transmittance is considered to be small.

A question of doping of nitrogen atoms to the film fabricated with $Ar+N_2O$ gas during the sputter deposition needs to be mentioned. The dissociation energy from N_2 molecules into two N atoms is 945 kJ/mol. This value is 6 times as large as the dissociation energy from N_2O molecules into N_2 molecules and O atom. Thus, it is considered that the amount of N_2 atoms or ions are relatively fewer during the sputter deposition,

and nitrogen doping to the film is considered to be little, which results in the higher optical transmittance in HfO_2 film.

3.2 Optical Transmittance for $(\lambda/4)$ HfO_2 / $(\lambda/4)$ SiO_2 DBR

Finally, Fig. 5 shows optical transmittance spectra for the DBR composed of $(\lambda/4)HfO_2$ and $(\lambda/4)SiO_2$ multilayer deposited with and without reactive gas of N_2O . An optical stop band appears at around 3.0 eV. The optical transmittance of the DBR deposited with the reactive gas of N_2O and that without the gas are compared. At the side of lower energy of the optical stop band, the optical transmittance improves from 92% to 98%. This value is close to the optical transmittance (> 99 %) of dielectric layer for high efficient micro-cavity. And at the side of higher energy of the optical stop band, the optical transmittance improves from 70% to 90%. Thus, we succeeded in improving the optical transmittance of the DBR.

4. CONCLUSION

We investigated the effect of N_2O gas on HfO_2 thin film and $(\lambda/4)$ HfO_2 / $(\lambda/4)$ SiO_2 DBR during reactive sputter deposition.

The efficient oxidation of hafnium material utilizing N_2O as a reactive gas during a sputter deposition was shown to improve the crystallization and surface roughness in deposited HfO_2 film. And the optical transmittance of HfO_2 thin film and $(\lambda/4)$ HfO_2 / $(\lambda/4)$ SiO_2 DBR were successfully improved.

Fig. 5 Optical transmittance spectra of $(\lambda/4)$ HfO_2 / $(\lambda/4)$ SiO_2 DBRs fabricated with Ar gas (---) and Ar+ N_2O gas (—) during the sputter doposition, respectively.

References

- [1] H. Kurisu, J. Horie, S. Yamamoto, M. Matsuura; *International J. Modern Physics B*, **15**, 3841-3845 (2001).
- [2] *Handbook of optical constants of solid*, edited by Edward D. Palik, Academic Press, Inc., (1985).
- [3] Y.-S. Lin, R. Puthenkovilakam, and J. P. Chang, *Appl. Phys. Lett.* **81**, 2041-2043, (2002).
- [4] J. P. Chang and Y.-S. Lin, *Appl. Phys. Lett.* **79**, 3666-3668 (2001).
- [5] M.F. Al-Kuhaili, *Optical Materials*, **27**, 383-387 (2004).

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