Measurements of Optical Parameters of $\gamma$-Mo$_2$N/Si(100) Thin Films

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Abstract. Molybdenum nitride films $\gamma$-Mo$_2$N/Si have been fabricated with reactive magnetron sputtering in (N$_2$ + Ar) gas mixture. Phase composition of the films has been defined with RHEED. Refractive index and extinction coefficient of $\gamma$-Mo$_2$N have been evaluated with laser ellipsometry at $\lambda = 632.8$ and 488.0 nm. Upper limit of $\gamma$-Mo$_2$N film thickness measurable with laser ellipsometry has been found as $\sim$80 nm.

Keywords: Laser Ellipsometry, Molybdenum Nitride, Thin Film, Optical Parameter

1. Introduction

Molybdenum nitride thin films exhibit high electrical conductivity and chemical stability and are promising candidate for using as Cu diffusion barrier and electrodes in microelectronics [1, 2]. Besides this, molybdenum nitrides show excellent hardness, catalytic ability and superconductivity effects. Different methods have been tested for fabrication of molybdenum nitride layers, including atomic layer deposition, ion assisted deposition, pulsed laser deposition, heavy nitrogen-ion implantation, chemical vapor deposition and nitriding Mo metal at high temperature. In comparison with other methods, reactive sputtering deposition seems be among most effective for transition metal oxide or nitride film fabrication because chemical and phase composition of the film is strongly dependent on the Ar-O$_2$-N$_2$ gas composition and deposition conditions. This technique is of special interest due to applicability to large-area substrates and good compatibility with electronic industrial technologies. As to reactive magnetron sputtering method, high quality films can be created even at relatively low substrate temperature because of plasma stimulation of ion interaction with substrate surface. The dependence of phase composition, mechanical and electrical properties of molybdenum nitride films on the $l = p(N_2)/[p(Ar) + p(N_2)]$ ratio and substrate temperature used in reactive sputtering deposition have been observed in several studies. At the same time, top surface structural characteristics are less studied while crystallinity and phase composition of molybdenum nitride films is a function of substrate temperature and nitrogen partial pressure. There is no information reported on optical properties of molybdenum nitrides though ellipsometry was mentioned as a method used for the film thickness control. Evidently, single wavelength ellipsometry is suitable and sensitive method for precise thin film thickness control and determination of physical parameters of nanometric films and bulk crystals [3].

This investigation presents the results of molybdenum nitride thin film fabrication by reactive magnetron sputtering deposition. The reactive gas mixture will be optimized to get $\gamma$-Mo$_2$N phase as main component of the film. Refractive index and extinction coefficient of $\gamma$-Mo$_2$N/Si film will be measured with laser null ellipsometry.
2. Experimental Methods

The molybdenum nitride films were deposited on Si (100) substrates by reactive dc magnetron sputtering of molybdenum metal (99.8%) target. The sputtering chamber was evacuated up to $\sim 5 \times 10^{-6}$ Torr prior to film-deposition and the working pressure was maintained at $\sim 1 \times 10^{-3}$ Torr with (N$_2$ + Ar) reactive gas mixture. The magnetron power was fixed at $W = 160$ W. The substrate temperature was selected to be in the range of $T = 375-580^\circ$C. Higher substrate temperatures were not used because partial nitrogen loss from molybdenum nitride was earlier detected at $T \sim 800^\circ$C. After the deposition the molybdenum nitride film was slowly cooled to room in reactive gas mixture inside the deposition chamber. Structural characteristics of the films were evaluated with reflection high energy electron diffraction (RHEED) under electron energy 50 keV. Optical parameters of the films were defined with laser ellipsometers LEF-2 and LEF-3M ($\lambda = 632.8$ and 488.0 nm). Ten molybdenum nitride film samples were fabricated at different $T$ and $l$ from the ranges $375 < T < 580^\circ$C and $31.8 < l < 100\%$ and tested with RHEED for crystallinity and phase composition. Two most representative samples fabricated at $T = 375^\circ$C and $l = 31.8\%$ (sample 1) and $T = 425^\circ$C and $l = 100\%$ (sample 2) were measured with laser ellipsometry.

Fig. 1. RHEED pattern of $\gamma$-Mo$_2$N film deposited at $W = 160$ W, $T = 425^\circ$C and $l = 100\%$ (sample 2).

3. Results and Discussion

RHEED observation shows a superposition of polycrystalline and amorphous phases for all deposition conditions. In Fig.1 the RHEED pattern is shown for the film fabricated at low $T$ and $l$. As it is evident, the intensity of hallo related to amorphous phase is relatively low and electron diffraction by small polycrystalline grains is dominant. The polycrystalline phase is identified as $\gamma$-Mo$_2$N (PDF 25-1366). For the comparison, in Fig.1 the RHEED pattern is demonstrated for the film created at higher $T$ in pure nitrogen gas. In this film the amorphous component is dominating. Residual crystalline phase is identified as $\gamma$-Mo$_2$N. As it appears, increasing of substrate temperature and higher nitrogen flow should be stimulating factors for molybdenum – nitrogen chemical bond formation. Under higher $T$ and $l$ the nucleation is so active that atomic ordering on the film surface is not finished and amorphous state is conserved. Earlier, crystallinity of $\gamma$-Mo$_2$N have been confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM) for the films deposited by reactive magnetron sputtering at $T = 120-500^\circ$C in different experiments. To decrease plasma action, in our magnetron set up as high target-substrate distance as $L = 20$ mm was used that ensure
minimum plasma heating of substrate surface. Under the conditions, crystalline $\gamma$-Mo$_2$N phase is dominant at $T = 375-425^\circ$C and amorphous component is prevailing at $T = 540-580^\circ$C. In the range $425 < T < 540^\circ$C the intensities of crystalline and amorphous components in RHEED patterns are similar.

Ellipsometric parameters $\Psi$ and $\Delta$ are defined by

$$\rho = R_p / R_s = \tan \Psi \exp (\imath \Delta).$$  \hspace{1cm} (1)

where $\rho$ is a complex reflection coefficient, $R_p$ and $R_s$ are Fresnel coefficients for $p$ and $s$ lightwave polarization. In the experiment the parameters $\Psi$ and $\Delta$ were measured for several values of angle of incidence $\phi$. Then, it has been found that equation (1) is fulfilled with measured $\Psi$ and $\Delta$ only in the framework of model of semi-infinite optical medium. This means that lightwave reflection is insensitive to the interface and substrate parameters and $\gamma$-Mo$_2$N/Si films fabricated in our experiment can be considered as optically thick. Ellipsometric parameters were measured for two samples. Optical constants calculated for these samples using model of semi-infinite optical medium are presented in Table 1. Fidelity of this reflection model for our samples has been confirmed by calculation of $\Psi(\phi)$ and $\Delta(\phi)$ functions shown in Fig. 2. Optical parameters of $\gamma$-Mo$_2$N are evidently dependent on technological conditions of film deposition and higher $n$ and $k$ are found for the film fabricated at lower nitrogen partial pressure and lower substrate temperature. It is interesting that negative dispersion has been observed for optical constants of $\gamma$-Mo$_2$N over the spectral range $\lambda = 632.8-488.0$ nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$n$</th>
<th>$k$</th>
<th>$\lambda$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.287</td>
<td>2.690</td>
<td>632.8</td>
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<tr>
<td></td>
<td>2.680</td>
<td>2.481</td>
<td>488.0</td>
</tr>
<tr>
<td>2</td>
<td>3.020</td>
<td>1.970</td>
<td>632.8</td>
</tr>
<tr>
<td></td>
<td>2.530</td>
<td>1.713</td>
<td>488.0</td>
</tr>
</tbody>
</table>

Laser ellipsometry is a nondestructive method of thin film thickness control. As to $\gamma$-Mo$_2$N/Si system, the range of film thickness $h$ measurable by ellipsometry with reasonable possible
error is limited by high optical absorption. The dependence of $\Psi$ on $\Delta$ calculated for different $h$ values is shown in Fig. 3. It is evident that $\gamma$-Mo$_2$N film thickness can be measured at $\lambda = 632.8$ nm within the range $0 < h < 85$ nm. This range is in a good relation with the limit $h \sim 80$ nm critical for ellipsometric control as reported for molybdenum nitride films created with atomic layer deposition.

![Graph showing dependence of $\Delta$ on $\Psi$](image)

Fig. 3. Dependence of $\Delta$ on $\Psi$ calculated for $\varphi = 70^\circ$ with $\gamma$-Mo$_2$N/Si film thickness as a parameter ($\lambda = 632.8$ nm). Optical constants of sample 2 were taken for the estimations. Film thickness values are given in nanometers.

4. Conclusion

The $\gamma$-Mo$_2$N films are fabricated with reactive magnetron sputtering of molybdenum metal target. Micromorphology and crystallographic properties of deposited layer were observed with SEM and RHEED methods. These give a basis for selection of adequate ellipsometric model and define the optical constants of $\gamma$-Mo$_2$N. Negative dispersion of refractive index and extinction coefficient of $\gamma$-Mo$_2$N has been found in visible spectral range.

References

