Defect and Diffusion Forum
ISSN: 1662-9507, Vol. 373, pp 237-240
doi:10.4028/www.scientific.net/DDF.373.237

Submitted: 2015-11-15
Revised: 2016-09-13
Accepted: 2016-09-13
Online: 2017-03-24

Positron Annihilation in TaN Thin Sputtering Films Prepared with Various N_2 Partial Pressures

Jiandang Liu[1, 2, a *], Bingchuan Gu[1, 2, b], Jiajie Fang[1, 2, c] and Bangjiao Ye[1, 2, d]

[1]State Key Laboratory of Particle Detection and Electronics, University of Science and Technology of China, China

[2]Department of Modern Physics, University of Science and Technology of China, China

[a]liujd@mail.ustc.edu.cn, [b]glacierg@mail.ustc.edu.cn, [c]yingfeng@ustc.edu.cn, [d]bjye@ustc.edu.cn

Keywords: TaN, thin films, slow positron beam.

Abstract. Tantalum nitride (TaN) thin films were deposited using magnetron sputtering method under different N_2/Ar ratio condition. Slow positron beam was used to analyze the microstructure of those films. The results show that the films which deposited at low N_2/Ar flow ratio contain more vacancy-like defects, and the corresponding S parameter is relatively large. The sheet resistance measurement displays that ohms-per-square greatly increase with increased N_2/Ar ratio. And the reasons could be related to nonstoichiometry-induced vacancies and lattice distortions.

Introduction

High frequency, high density and low power consumption in modern very large-scale integrations (VLSI) are limited in speed by the large increasing interconnect RC delay and interline crosstalk noise. Although new interconnect technology becomes available, such as aluminum interconnect lines were replaced by Cu-interconnects and low-*k* dielectric materials have been inserted to address the additional RC delay reduction. It has been found that the devices with low-*k* dielectric materials usually have better RC value to increase speed and to reduce interline crosstalk noise. But copper diffusion into SiO_2 or other low-*k* siliceous materials is easy forming in copper damascene process, which can form leakage paths and cause electrical failure. Thus, thin diffusion barriers are needed to prevent intermixing of Cu with the insulating substrate. TaN has received the most attention owing to its high thermal stability and excellent barrier capability against Cu diffusion [1]. And it is also a primary candidate material for diffusion barrier coating in VLSI electronics industry.

Defect density distributions play an important role in coating process control. Non-uniformity or existence of vacancies in intermediate layers may seriously affect its impervious ability. Cu atoms diffusion can occur by the motion of vacancies or impurities, and it can also cause the necessary lattice distortion. Thus it is important to understand the defect distribution in TaN coating films. Many studies [2] have focused on the advanced manufacture or processing techniques in order to economically produce high quality barrier films. Analysis of the influence of environmental parameters is also an important branch in the field of barrier materials research.

Positron annihilation spectroscopy (PAS) is a sensitive probe for studying the electronic structure of defects in solids. Non-destructive PAS measurements can detect the relative vacancy concentrations as low as 10^{-7} per atom, and may saturation at 10^{-4} per atom. Positron annihilation characteristics depend on the type of defect in which the positron is trapped. Hence it is possible to a large extent to differentiate between different types of defects, and from the rates with which the defects trap positrons, defect concentrations can be derived [3]. In this study, magnetron sputtering method was used to deposit the TaN barrier films under different N_2/Ar ratio condition. Slow positron beam technique is employed to obtain the defect depth profile, which can adjust the positron energy in a range of a few eV to several tens of keV. To analyze the obtained Doppler-broadening energy spectrum, the line-shape parameter S is introduced which is defined as the ratio of the area of a suitably selected central region of the energy spectrum versus the entire area. And the influence of N_2 partial pressure were obtained.

Experiments

TaN thin films have been deposited onto glass substrates in Ar (99.99%) by a DC reactive magnetron sputter method. The substrates were firstly polished, cleaned and dried in order to remove residual oil and other contaminants. The sputtering target is tantalum with the purity of 99.9%. The power of Ta target was fixed at 100 W. The Ar and N_2 flow rates were controlled by two separate flow meters. In this experiment, four different deposition conditions were tried, and the N_2 flow was set to 5ml/min、15ml/min、25ml/min and 50ml/min respectively. Each film is deposited for 3 minutes at a deposition rate not exceeding 50nm/min. And four corresponding TaN thin films (namely 1#, 2#, 3# and 4#) were deposited.

The depth profiles of defects in TaN films were measured using a variable energy positron beam which can changes positron energy from 0.25 keV to 20 keV. The sample chamber has a vacuum below 10^{-5}Pa. The high-purity germanium (HPGe) detector with typical energy resolution (FWHM) of 1.2 keV for 514 keV γ-rays of ^{85}Sr was used to measure the Doppler broadening spectra. The total net spectrum count for each incident energy reached over 2×10^5. The line-shape parameter S was used to analyze the Doppler broadening spectra. In this process, the parameter S is defined as the ratio of the annihilation events of the central region (511 ± 1 keV) to the total area of 511 keV annihilation peak. And all S-E curves were fitted using VEPFIT code [4].

Results and discussion

The typical S values of the TaN thin films versus the incident positron energy E are illustrated in Fig. 1. The scatter plots are the experiment values and the solid curves are the corresponding fitting results. The mean implantation depth Z is also shown at the top horizontal axis. The feature of S-E curves shows some similarities through analysis of typical annihilating behaviors of incident positron and its character in diffusion process. At lower incident positron energies, positrons can be trapped in the surface image potential or in surface defects, and the contribution to positronium formation from backscattered positrons becomes large. As a result, the S-values at the surface are larger than that within TaN thin films. As the incident energy increases, more positrons annihilate in TaN films and less non-thermalized positrons backscattering out of the samples. This variation leads to the rapid descent of S values down to low altitude. At higher energies, more positrons reach the glass substrates and the S parameters are gradually enhanced. In this case, all of the annihilation information belongs to the referential substrates.

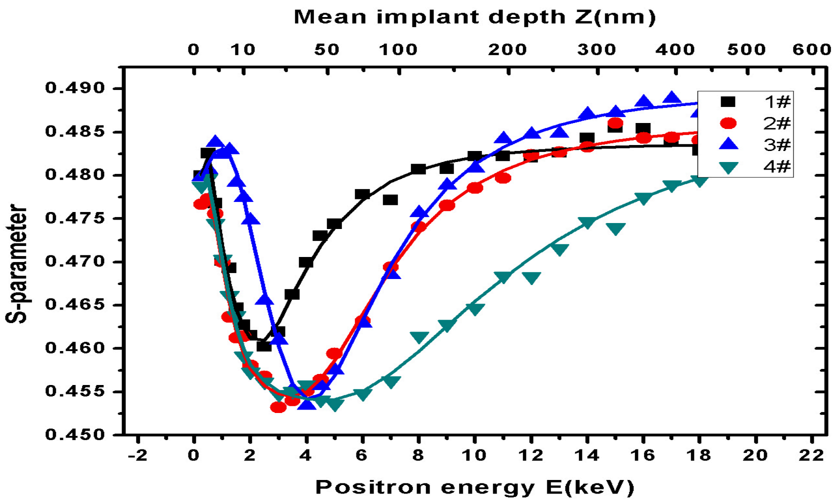

Figure 1 S parameters as a function of incident positron energy E for four TaN thin films. The solid curves are the fitted results by VEPFIT.

The VEPFIT was then used to obtain the S-value and effective diffusion length in different TaN films. Table 1 summarizes the relationship between S parameter and effective positron diffusion length for all samples studied basing on multi-layer model. According to the experimental data, the positron implantation profile measured in Fig. 1 involves at least three components: positrons on the surface, positron in the bulk TaN film and positron in the glass substrate. Therefore, the measured S parameter can be formulated in the form S=SsFs+SbFb+SgFg, where Ss, Sb and Sg are the S parameters for sub-surface region, TaN bulk and glass substrate respectively, while Fs, Fb and Fg denote the fraction of positrons annihilated in the sub-surface region, TaN film and glass substrate respectively.

Table 1 The fitted S-value and effective diffusion length L_{eff} of TaN thin films.

Sample number	N_2 flow [ml/min]	S	L_{eff} [nm]
1#	5	0.4643	30.1
2#	15	0.4614	35.4
3#	25	0.4598	63.1
4#	50	0.4560	91.4

It can be seen from the Table 1 that S parameter in the TaN films decreases along with the N_2 partial pressure increases. W.H. Lee et al. [5] studied the deposition rate, chemical composition, and crystalline microstructure of TaN films deposited on silicon substrates by radio frequency (RF) reactive sputtering of Ta in different nitrogen partial pressure, and found the N/Ta ratio increases steeply at first and, then, becomes saturated as the N_2/Ar flow ratio increases. Deposition rates at lower N_2 partial pressures are usually larger than that at a higher N_2 partial pressure. At low N_2 partial pressures, the contribution to vacancy-like defects mainly arises from the nonstoichiometric variations. Therefore, the film which deposited at low N_2/Ar flow ratio contains more vacancy defects, a small increase in the N_2 partial pressure changes the defect structure significantly, and the corresponding S parameter becomes smaller. As the N_2 partial pressure increases, the more collisions occur between Ta and N atoms, the more dense TaN films is deposited. As a result, the S parameter gradually decreases with increasing the N_2/Ar flow ratio.

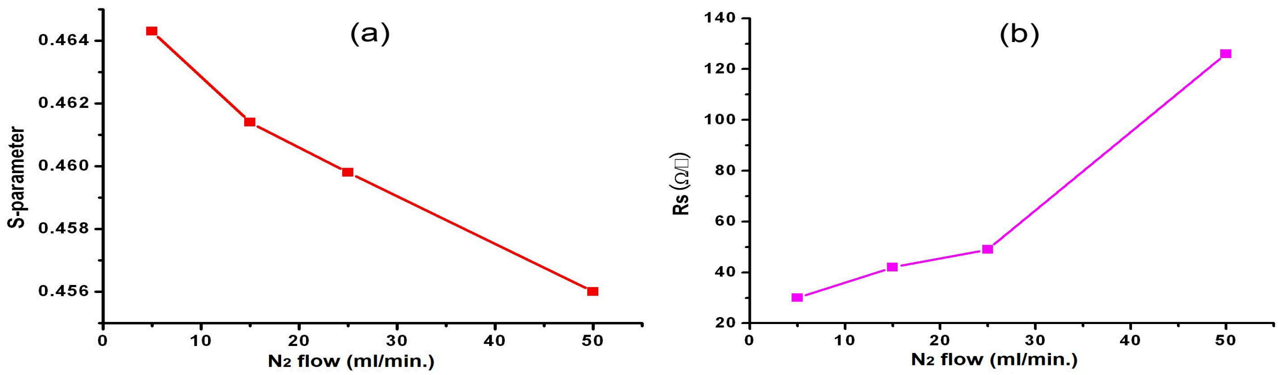

Figure 2 (a) S parameter and (b) sheet resistance as a function of N_2 flow.

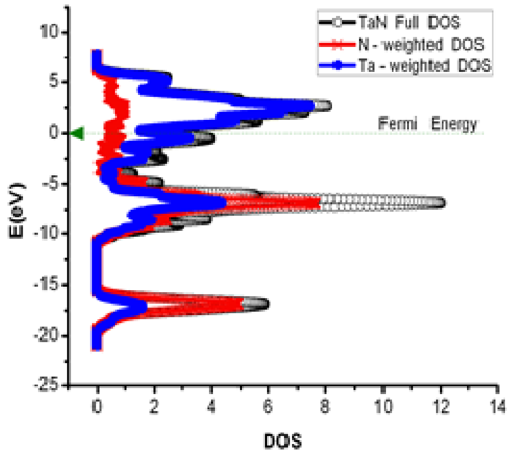

Figure 3 Calculated total and partial DOS of TaN using the pseudopotential plane-wave method.

The properties of materials are strongly influenced by the presence of defects or imperfections. The variation of the sheet resistance of TaN films with the N_2 partial pressure in the sputtering plasma is also shown in Fig. 2. It can be clearly seen that the change trend of sheet resistance is in good agreement with the evolution of the crystal structure. This behavior can be understood in the terms of vacancy-like defects variations. Increasing the N_2/Ar flow ratio resulted in an increase in stoichiometric ratio, which is causing decreased the vacancy-like defects. But other defect types may arise during the processing of film growth. For example, grain boundaries would attract more impurity atoms at lower deposition rate, and the transport properties of these conduction electrons are strongly influenced by scattering at dislocation cores. Additionally, a single grain boundary can lead to a million-fold increase in resistance over single crystals [6, 7].

The electron density of states (DOS) of solids is basically determined by its electron structure. Fig. 3 shows total and partial DOS of TaN using the pseudopotential plane-wave method. It shows the conductive properties of TaN, and it should also be noted that the total density of states at the Fermi level mainly originates from 3d state of Ta, which in turn can affect the resistivity. Thereafter, resistance can also be increased duo to lattice distortions caused by non-stoichiometric variation.

Conclusion

TaN thin films was deposited using a DC reactive magnetron sputter method. The microstructure of sputtered thin TaN films is strongly correlated with the deposition conditions. The defect depth profile in TaN films was studied with slow positron beam. The results demonstrate the distinct changes of S-parameter and positron effective diffusion length with the samples deposited at different N_2/Ar flow ratios. The films which deposited at low N_2/Ar flow ratio contain more vacancy-like defects, and the sheet resistance is closely related to nonstoichiometry-induced defects.

Acknowledgements

The work was supported by National Natural Science Foundation of China under the grant No. of 11175171 and 11475165.

References

[1] S. Mardani, H. Norström, U. Smith, J. Olsson, S. Zhang, Influence of tantalum/tantalum nitride barriers and caps on the high-temperature properties of copper metallization for wide-band gap applications, Microelectronic Engineering 137 (2015) 37-42.

[2] J. C. Tsao, C. P. Liu, H. C. Fang, Y. L. Wang, How tantalum proceeds phase change on tantalum nitride underlayer with sequential Ar plasma treatment, Mater. Chem. Phys. 137 (2013) 689–693.

[3] M. Eldrup. Positron Methods for the Study of Defects in Bulk Materials. Journal de Physique IV Colloque, 05 (1995) C1-93.

[4] A. van Veen, H. Schut, M. Clement, J. M. M. de Nijs, A. Kruseman, M. R. IJpma, Appl. Surf. Sci. 85 (1995) 216.

[5] W. H. Lee, J. C. Lin, C. P. Lee, Characterization of tantalum nitride films deposited by reactive sputtering of Ta in N_2/Ar gas mixtures, Mater. Chem. Phys. 68.1 (2001) 266-271.

[6] S. Thiel, C. W. Schneider, L. Fitting Kourkoutis, D. A. Muller, N. Reyren, A. D. Caviglia, S. Gariglio, J.-M. Triscone, J. Mannhart, Electron Scattering at Dislocations in $LaAlO_3$/$SrTiO_3$ Interfaces, Phys. Rev. Lett. 102 (2009) 046809.

[7] P. Y. Huang, C. S. Ruiz-Vargas, A. M. van der Zande, W. S. Whitney, M. P. Levendorf, J. W. Kevek, S. Garg, J. S. Alden, C. J. Hustedt, Y. Zhu, J. Park, P. L. McEuen, D. A. Muller, Grains and grain boundaries in single-layer graphene atomic patchwork quilts, Nature 469 (2011) 389.