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Barrier properties of Ta–Si–N films in Ag-and Au-containing metallization

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Abstract

Thin films of Ta–Si–N were deposited by r.f. magnetron sputtering in Ar/N_2 gas mixture. Film composition was controlled in large range by changing the r.f. power and nitrogen flow rate. The scope of the study was to determine the relationship between the process parameters and the features of composite films. The effectiveness of the Ta–Si–N films as a diffusion barrier between Ag-, Au-overlayer and the (1 0 0)-oriented GaAs substrate has been studied. Sheet resistance measurements, Rutherford backscattering spectrometry and atomic force microscopy showed that a 100 nm thick $Ta_{34}Si_{25}N_{41}$ film effectively suppress a metallurgical interaction between Ag and GaAs under annealing in an Ar ambient up to 750°C for 5 min. For Au overlayer excellent barrier performance was observed up to 800°C.
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1. Introduction

The stability of thin film diffusion barriers in semiconductor high-temperature metallization is essential for successful device performance. Good diffusion barriers promote the low diffusitivity of metals, low resistivity and the high chemical stability of the layer. Electrically conducting amorphous and near-amorphous thin films composed of a transition metal, silicon, and nitrogen (TM–Si–N) were considered as the most effective diffusion barrier due to their high crystallization temperature and lack of grain boundaries in an amorphous structure eliminating fast diffusion paths [1–3]. They can be structurally amorphous, electrically conducting and chemically inert depending on the condition of deposition [1,4,5], on their composition [6,7], and post-deposition treatment.

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In this work, we have investigated the influence of the deposition parameters on the material properties and thermal stability of amorphous Ta–Si–N thin films and their performance as diffusion barriers between Ag-, Au-overlayer and GaAs. This study was focused on the effect of deposition processes and nitrogen content in Ta–Si–N thin films on physical properties and the diffusion barrier performance.

2. Experimental

Ta–Si–N films were deposited by reactive r.f. magnetron sputtering from a Ta_5Si_3 target (7.5 cm dia. and 99.95% purity), onto unheated substrates at the target-to-substrate distance of 6.5 cm. The base pressure in the vacuum chamber was 1×10^{-6} mbar. Sputter deposition was conducted in a gas mixture of N_2 and Ar. N_2/Ar flow ratio (from 0% to 12%) and the total gas pressure of 4×10^{-3} mbar were adjusted by mass flow controllers and monitored with capacitive manometer in a feedback loop. The samples were prepared at power ranging from 100 to 200 W.

Semi-insulating GaAs (1 0 0)-oriented wafers were used as the substrates. Prior to loading into the sputtering chamber, the wafers were degreased in organic solvents (trichloroethylene, acetone, methanol), etched in NH_4OH:H_2O_2:H_2O = 20:7:973, rinsed in de-ionized H_2O, dipping in NH_4OH:H_2O = 1:10 for 15 s, and blown dry with N_2.

The resistivities of thin films were assessed from sheet resistance (R_s) measurements by a four-point probe. Tencor α-step profilometer was applied to determine the thickness of the deposited films. The electrostatic accelerator Lech at SINS Warsaw was applied to perform the Rutherford backscattering spectrometry (RBS) using the 2 MeV He^+ ions. The content of nitrogen was measured by the $^{14}N(d,\alpha)^{12}$ nuclear reaction analysis method (NRA) [8]. Kinetic energy spectra of backscattered ions and of helium nuclei produced in the reaction were used with the RUMP code [9] for the elemental analysis. Microstructural analysis was performed by X-ray diffraction method (XRD), while surface morphology and the root-mean-square (RMS) roughness were examined using atomic force microscopy (AFM).

To determine the barrier properties of Ta–Si–N films in Ag, Au/barrier/GaAs systems, 115 nm thick Ag (90 nm thick Au) films were deposited by d.c. magnetron sputtering onto about 100 nm thick barrier layers. Next, samples were annealed for 5 min in an Ar ambient at temperatures up to 800°C.

3. Results and discussion

Table 1 presents a comparison of the features of the sputtered Ta–Si–N films at various N_2/Ar gas flow ratios and different power of deposition. The deposition rates of Ta–Si–N films depend little on the N_2/Ar gas flow ratios at the total sputtering gas pressure of 4×10^{-3} mbar.

The composition changed from $Ta_{58}Si_{21}N_{21}$ to $Ta_{33}Si_{23}N_{44}$, while the N_2/Ar gas flow ratios

Table 1
Properties of the Ta–Si–N films sputtered at the r.f. power range of 100–200 W and the N_2/Ar flow ratio of 2–12%

N_2/Ar flow ratio (%)	Power (W)	Deposition rate (nm/min)	Composition	Resistivity (10^{-3} Ω cm)	Roughness RMS (nm)
2	200	34	$Ta_{58}Si_{21}N_{21}$	0.334	0.658
5	200	34	$Ta_{53}Si_{20}N_{27}$	0.359	0.697
10	200	38	$Ta_{34}Si_{25}N_{41}$	0.810	0.374
12	200	38	$Ta_{33}Si_{23}N_{44}$	1.420	0.761
8	100	21	$Ta_{29}Si_{22}N_{49}$	20	0.328
8	150	31	$Ta_{38}Si_{20}N_{42}$	1.1	1.235
8	200	39	$Ta_{40}Si_{25}N_{35}$	0.55	0.496

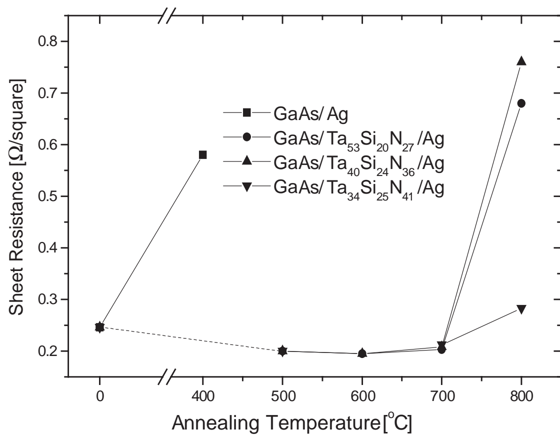

Fig. 1. Sheet resistance of the GaAs/Ag and GaAs/Ta–Si–N/Ag samples annealed in Ar ambient at temperature range of 400–800°C for 5 min.

increased from 2% to 12% at power of 200 W. However, the amount of Si component was modified in the range of 21–25% only. When the r.f. power was increased from 100 to 200 W, the nitrogen content in the film reduced at the N_2/Ar flow ratio of 8% and the deposition rate increased two times, because nitrogen had less time to react and to be incorporated into the film. When the nitrogen concentration in film was increased, the Ta/Si ratio in the film decreased.

The electrical resistivity presented in Table 1 was measured on 100 nm thick films. The resistivity was changed in a similar way as composition. The resistivity increased when the nitrogen increased in composition: $0.334 \times 10^{-3}\,\Omega\,\text{cm}$ for $Ta_{58}Si_{21}N_{21}$ (at 2% of N_2/Ar ratio and 200 W), and $20 \times 10^{-3}\,\Omega\,\text{cm}$ for $Ta_{29}Si_{22}N_{49}$ (at 8% of N_2/Ar ratio and 100 W).

The AFM measurements did not show the correlation of the roughness change vs. the composition, and process parameters. The surface of deposited films was rather smooth and the RMS values were in range 0.3–1.2 nm.

The X-ray analysis of Ta–Si–N films did not show any diffraction peak, except the GaAs (1 0 0) substrate, so all films reported in this paper were X-ray amorphous as deposited.

According to the future requirements for the semiconductor devices a films resistivity value around $1 \times 10^{-3}\,\Omega\,\text{cm}$ is required [10]. Then, the films with resistivity below of this value were tested as diffusion barriers between Ag-, Au and GaAs using AFM, RBS, and sheet resistance measurement.

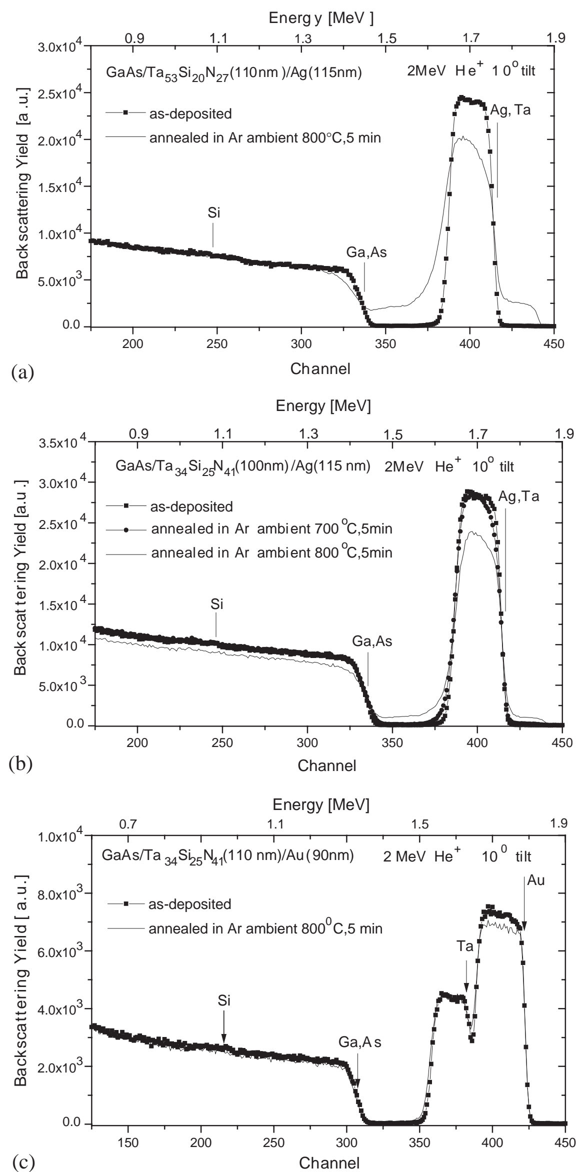

Fig. 2. The 2 MeV He^+ backscattering spectra: (a) GaAs/$Ta_{53}Si_{20}N_{27}$/Ag sample before and after annealing at 800°C; (b) GaAs/$Ta_{34}Si_{25}N_{41}$/Ag sample before and after annealing at 700°C and 800°C and (c) GaAs/$Ta_{34}Si_{25}N_{41}$/Au sample before and after annealing at 800°C.

The sheet resistance of various GaAs/Ta–Si–N/Ag samples as a function of annealing temperature is shown in Fig. 1. The initial sheet resistance of $R_s = 0.25\,\Omega/\square$ of all the as-deposited samples corresponded to the Ag film resistivity of about $2.875\,\mu\Omega\,cm$. This value exceeds the resistivity of pure bulk silver ($2\,\mu\Omega\,cm$ [11]), which is typical for thin films.

The low eutectic temperature of the Ag-Ga system (540°C) and the observation that a GaAs substrate reacted interfacially with a directly overlaying Ag film after annealing already at 400°C explained the rapid increase of the Ag metallization resistance [11]. For all GaAs/Ta–Si–N/Ag samples, the first annealing step at 500°C reduced R_s by about 20%. This reduction was not caused by metallurgical or chemical reactions. It may be explained by change of grains size in the silver layer.

The sheet resistance were nearly unchanged up to an annealing temperature of 700°C, for all GaAs/Ta–Si–N/Ag samples (Fig. 1). An increase of sheet resistance for films with nitrogen concentration from 27% to 35% after annealing at 800°C indicated that the diffusion barriers fail. The backscattering spectra of the GaAs/$Ta_{53}Si_{20}N_{27}$/Ag sample before and after annealing at 800°C is shown in Fig. 2a. It was clear that the barrier, approximately 110 nm thick, had failed during annealing at 800°C. Then R_s values of the GaAs/$Ta_{34}Si_{25}N_{41}$/Ag sample increased slightly. Backscattering spectra of this sample, as-prepared and annealed at 700°C, showed no detectable differences at the two interfaces of the barrier layer (Fig. 2b). However, after annealing at 800°C an interaction between the silver overlayer and the diffusion barrier was observed.

The backscattering spectrum of GaAs/$Ta_{34}Si_{25}N_{41}$/Au sample for comparison with Ag metallization is shown in Fig. 2c. The intermediate amorphous $Ta_{34}Si_{25}N_{41}$ film totally prevented the

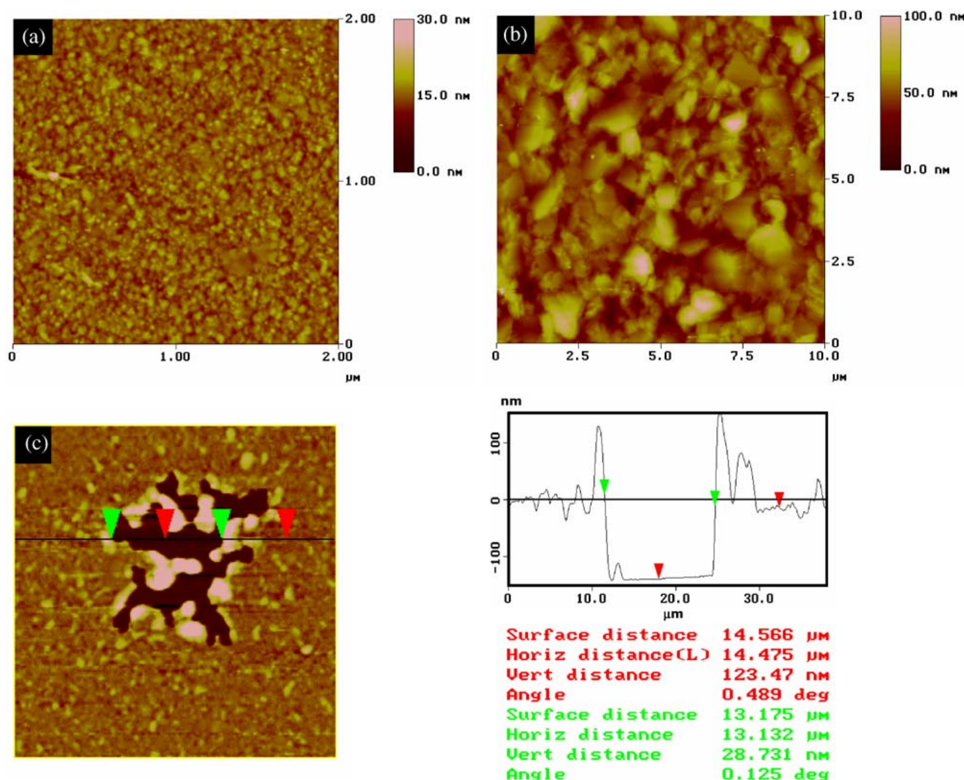

Fig. 3. AFM surface image of GaAs/$Ta_{34}Si_{25}N_{41}$/Ag samples: (a) as deposited, (b) and (c) annealed at 800°C in an Ar ambient for 5 min. Analyzed area in case (c) was of $40 \times 40\,\mu m^2$.

interaction between Au and GaAs after annealing at 800°C, which has been reported in [12].

Surface morphologies of $GaAs/Ta_{34}Si_{25}N_{41}/Ag$ samples before and after annealing at 800°C is shown in Fig. 3. The surface of as-deposited films was smooth with RMS roughness about 1 nm. Upon thermal annealing, the RMS roughness increased to 7 nm and coincided with the growth of grains of about 500 nm. However, the AFM image showed the place of dip craters in Ag layer annealed at temperature of 800°C. The average amount of craters in this layer was about 500 per 1 mm^2. The depth of these craters was in the range of the thickness of the Ag layer. However, the area occupied by the craters was too small to cause a change of sheet resistance and the backscattering spectra.

4. Conclusion

Amorphous Ta–Si–N thin films of various compositions were deposited by r.f. magnetron sputtering and tested as a diffusition barrier for Ag- and Au-metallization. The N_2/Ar gases flow ratios and the applied power strongly influenced on the composition and resistivity of the layer. The electrical resistivity and thermal stability was increased with increasing nitrogen content in the films. The most thermal stable barrier layer had about 40 at% nitrogen. The 100 nm thick $Ta_{34}Si_{25}N_{41}$ film showed excellent barrier property and prevented the interaction between Ag and GaAs up to 750°C. This layer also showed excellent barrier property preventing the interaction between Au and GaAs up to 800°C.

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