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Amorphous Ta–Si–N diffusion barriers on GaAs

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Abstract

Binary Ta–Si and ternary Ta–Si–N films of various compositions were deposited by reactive r.f. magnetron sputtering from Ta_5Si_3 target and tested as diffusion barriers between GaAs and Au. All as-deposited films were amorphous and conducting. Their resistivity and crystallisation temperature increased with increasing nitrogen. While nitrogen-free Ta–Si films crystallised at 600 °C, for the most stable $Ta_{34}Si_{25}N_{41}$ layers crystallisation occurred above 900 °C. 100 nm thick $Ta_{34}Si_{25}N_{41}$ films prevented interaction between Au and GaAs during annealing at temperatures up to 800 °C.

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Keywords: Diffusion barrier; Metallisation; Thin films; GaAs

1. Introduction

The achievement of thermally stable metallisation is crucial for the performance and reliability of any semiconductor device targeting high power/high frequency applications. The remarkable breakthrough in this domain has been achieved by Nicolet and co-workers, who studied the growth and properties of conducting amorphous or near-amorphous compounds, highly metastable against crystallisation. These materials are composed of three elements: (i) an early transition metal (TM) as Ta, Ti, Mo, or W; (ii) silicon (boron or carbon); and (iii) nitrogen (carbon or boron) [1–4]. The systems the most investigated are TM (Ti, Ta, Mo)–Si–N, and the corresponding results indicate their excellent thermal stability due to the fact that amorphous to crystalline phase transition takes place above 800 °C. The exceptional combination of properties such as fairly low resistivity, amorphous, thus free of fast diffusion paths, microstructure as well as high thermal and chemical resistance makes them materials of choice for diffusion barriers in metallisation systems to semiconductor devices.

In this work, we have investigated the deposition processes and thermal stability of amorphous Ta–Si and Ta–Si–N thin films and their performance as diffusion barriers between Au and GaAs. The major concern of this study was the effect of nitrogen content in Ta–Si–N thin films on microstructural, electrical and barrier properties.

2. Experimental

Ta–Si–N films were deposited by reactive r.f. magnetron sputtering from a Ta_5Si_3 target (7.5 cm in diameter and 99.95% purity), onto unheated substrates. The target-to-substrate distance was 6.5 cm. The base pressure in the vacuum chamber was 8×10^{-7} Torr. Sputter deposition was conducted in a gas mixture of N_2 and Ar. N_2/Ar flow ratio (from 0 to 20%) and the total gas pressure of $3–4\times10^{-3}$ Torr were adjusted by mass flow controllers and monitored with capacitive manometer in a feedback loop. The target power was 200 W. The thickness of Ta–Si–N films was approximately 100 nm.

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Table 1
Properties of Ta–Si–N thin films deposited by reactive sputtering from Ta_5Si_3 target

Thin Films	N_2 flow (sccm)	Ar flow (sccm)	Deposition rate (nm/min)	Ration Ta:Si:N by RBS	Resistivity ($\mu\Omega$ cm)	Stress (GPa)	Atomic density (10^{22} cm^{-3})
Ta–Si	–	130	34	67:33	295	−1	6.4
Ta–Si–N	2	100	34	58:21:21	334	−1.3	6.9
Ta–Si–N	5	100	33.8	53:20:27	359	−1.5	7.4
Ta–Si–N	8	100	31.5	40:24:36	416	−1.1	9.3
Ta–Si–N	10	100	38.3	34:25:41	810	−1.1	8.6
Ta–Si–N	12	100	38	33:23:44	1420	–	8.4
Ta–Si–N	20	100	37.8	28:22:50	38 250	–	9

The substrates were semi-insulating GaAs (100) oriented wafers. Before deposition of metallisation the wafers were degreased in hot organic solvents, etched in $NH_4OH:H_2O_2:H_2O = 20:7:973$ for 1 min., rinsed in H_2O DI, dipped 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 thin films. Stress measurements were performed with Tencor FLX 2320 system. The film composition was analysed by Rutherford backscattering spectrometry (RBS) using 2 MeV He^+ ions. The spectra were fitted with RUMP simulation code for quantification of the composition. Microstructural analysis was performed by X-ray diffraction method (XRD), while surface morphology and roughness were examined using atomic force microscopy (AFM).

For thermal stability studies, Ta–Si and Ta–Si–N films were furnace annealed at temperatures from the range 400–1000 °C, for 5 min in Ar ambient. To determine the barrier properties of Ta–Si–N films in GaAs/barrier/Au system, 90 nm thick Au films were deposited onto 100 nm thick barrier layers. Next, samples were annealed for 5 min. at temperatures up to 800 °C in Ar ambient.

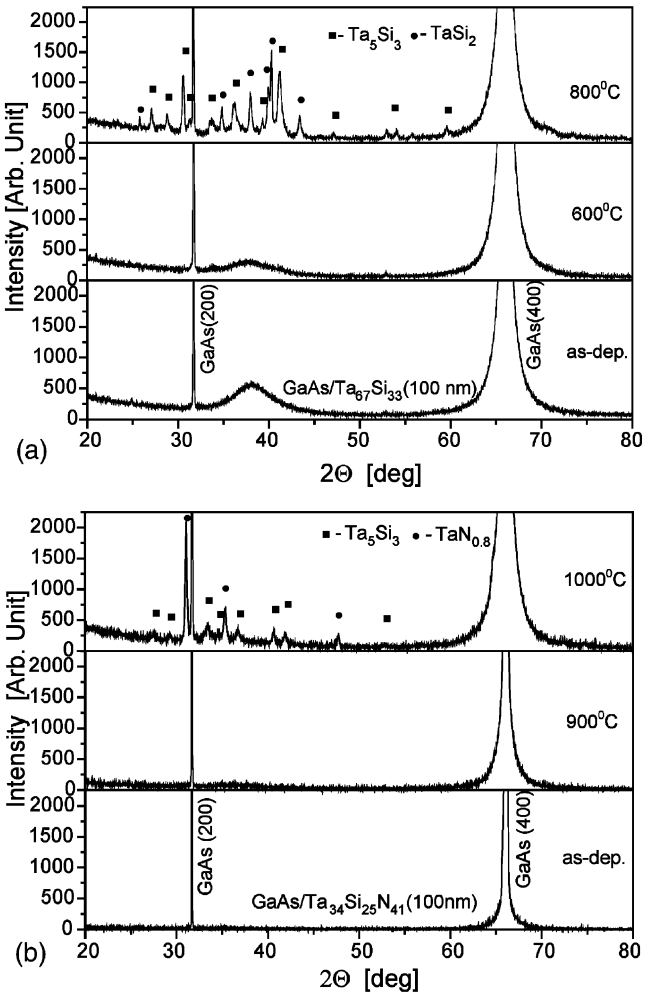

Fig. 1. X-Ray diffractograms of (a) $GaAs/Ta_{67}Si_{33}$ and (b) $GaAs/Ta_{34}Si_{25}N_{41}$ samples before and after annealing.

3. Results and discussion

The fundamental properties, i.e. composition, resistivity, stress and density of 100 nm thick Ta–Si and Ta–Si–N films deposited with increasing amount of nitrogen are listed in Table 1. The deposition rate of pure Ta–Si films was approximately 35 nm/min and remained constant with rising N_2 flow. The Ta/Si ratio in nitrogen-free Ta–Si film is 2, as compared to 1.67 in Ta_5Si_3 target material, which indicates preferential sputtering with Ta enrichment. By adding nitrogen to the sputtering plasma, this ratio increased to the maximum value of 2.65 for 5% of N_2. For higher nitrogen amounts, the decrease of Ta content in Ta–Si–N films was noted.

All analysed Ta–Si–N films on GaAs substrates were compressively stressed. The stress increased from 1 GPa for nitrogen-free film to 1.5 GPa for Ta–Si–N layer deposited in plasma containing 5% of N_2. For higher nitrogen amounts the reduction stress to ~1 GPa has been observed.

The compositions and atomic densities of Ta–Si–N films deposited at various N_2/Ar flow ratios were derived from RBS analysis with an estimate error of

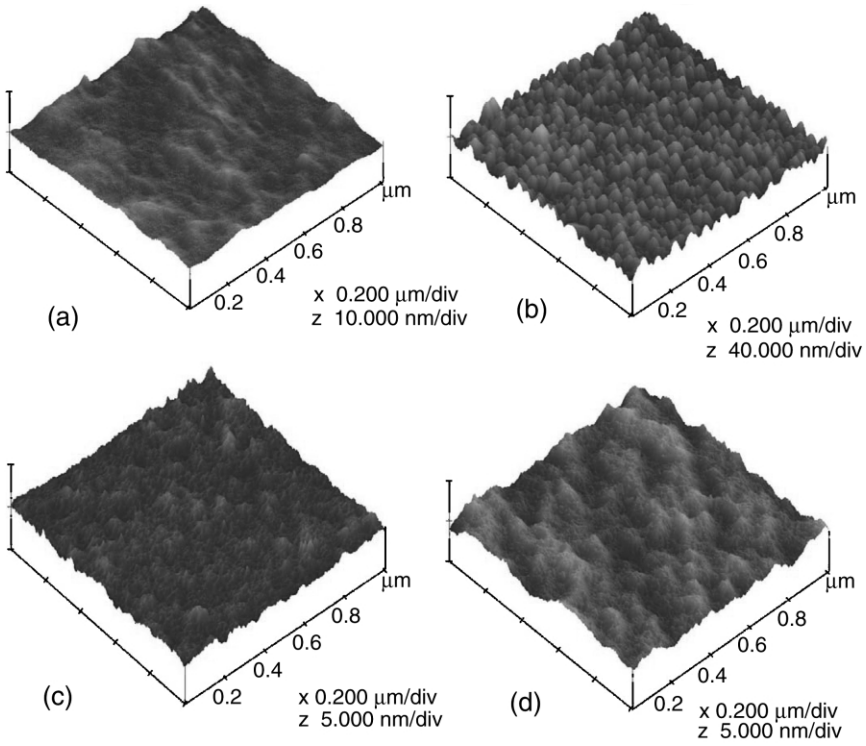

Fig. 2. AFM surface image of $Ta_{67}Si_{33}$ samples (a) as-deposited, (b) annealed at 700 °C for 5 min., and $Ta_{34}Si_{25}N_{41}$ samples (c) as-deposited, (d) annealed at 900 °C for 5 min.

±5%. By rising N_2/Ar flow ratio, the nitrogen content and atomic density of Ta–Si–N films increased, while the content of Ta and Si diminished. As N_2/Ar flow ratio changed from 0 to 20%, the amount of nitrogen in ternary films raised from 0 to 50% and the atomic density increased 1.5 times.

The resistivity of pure $Ta_{67}Si_{33}$ film was 295 μΩ cm and rose slowly up to 810 μΩ cm for the ternary $Ta_{34}Si_{25}N_{41}$ film. Further increase in nitrogen concentration caused rapid resistivity increase. For contacts of submicron dimensions, barriers with bulk resistivities below 1 mΩ cm are desirable [4].

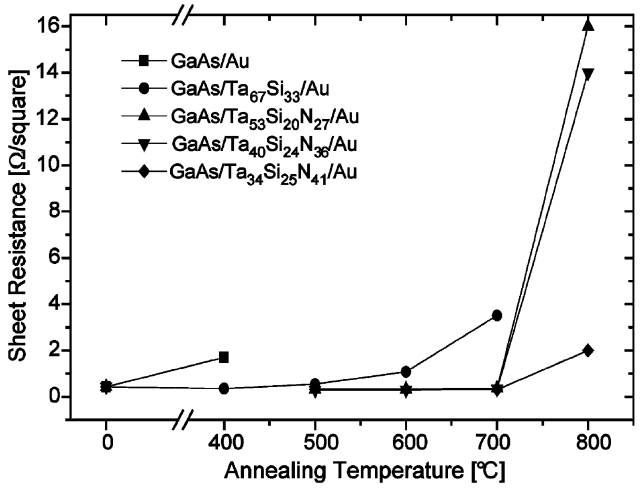

Fig. 3. Sheet resistance of GaAs/Au and GaAs/Ta–Si–N/Au samples annealed at temperatures from the range 400 to 800 °C.

All as-deposited films described in this article were amorphous, as identified by X-ray analysis. Fig. 1 shows X-ray diffraction spectra of the as-deposited and annealed $Ta_{67}Si_{33}$ and $Ta_{34}Si_{25}N_{41}$ films. As shown in Fig. 1a, apart of two sharp peaks corresponding to GaAs substrate, the broad peak centred approximately $2\Theta = 38–39°$ for the as prepared $Ta_{67}Si_{33}$ film is indicative of an amorphous film as earlier reported in the literature [5,6]. This amorphous nature of this nitrogen-free layer was preserved up to 600 °C. At higher temperature anneals the film structure appears to be polycrystalline and composed of two phases: Ta_5Si_3 and $TaSi_2$.

The spectra of $Ta_{34}Si_{25}N_{41}$ film show no obvious peaks up to 900 °C annealing (Fig. 1b). $Ta_{34}Si_{25}N_{41}$ film crystallised at 1000 °C and formed Ta_5Si_3 and $TaN_{0.8}$.

Fig. 2 shows surface morphologies of $Ta_{67}Si_{33}$ and $Ta_{34}Si_{25}N_{41}$ films before and after annealing. The surface of as-deposited films is very smooth with mean roughness approximately 0.25 nm. In the case of the $Ta_{67}Si_{33}$ layer, no noticeable change was observed up to 600 °C annealing. The roughness increased to 3.5 nm after heat treatment at 700 °C and coincided with the growth of 60 nm long crystallites (Fig. 2b). In contrast,

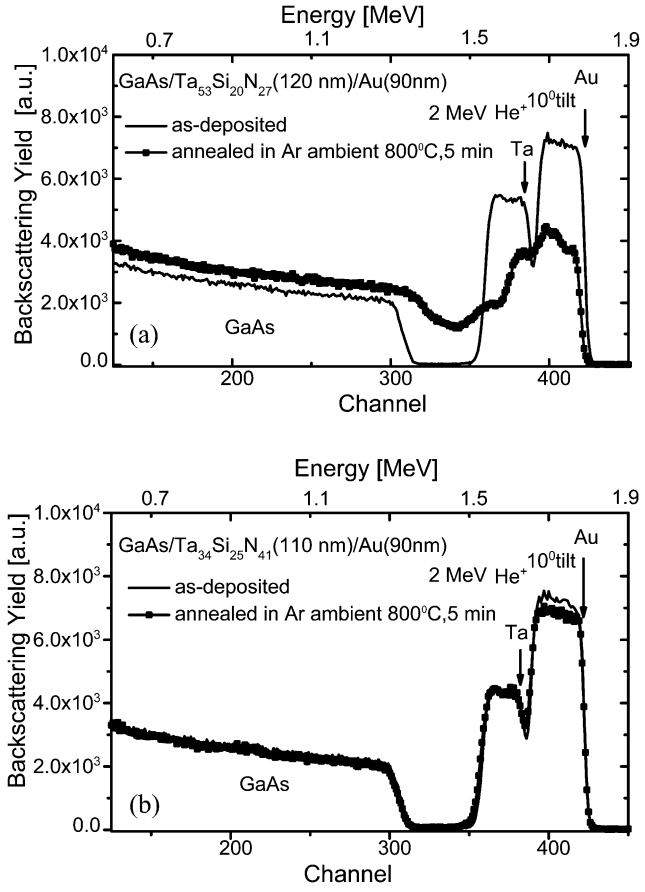

Fig. 4. 2 MeV He^+ backscattering spectra of samples before and after annealing in Ar at 800 °C for 5 min: (a) GaAs/$Ta_{53}Si_{20}N_{27}$/Au; (b) GaAs/$Ta_{34}Si_{25}N_{41}$/Au.

the surface of $Ta_{34}Si_{25}N_{41}$ film remained very smooth, with a roughness of 0.35 nm, even after annealing at 900 °C (Fig. 2d).

The thermally induced transformations in the microstructure of Ta–Si and Ta–Si–N films are also reflected in resistivity measurements. The resistivity decreased from the value of 295 μΩ cm for the as-deposited $Ta_{67}Si_{33}$ film to 165 μΩ cm after annealing to 800 °C. In the case of ternary $Ta_{34}Si_{25}N_{41}$ layer, the resistivity drop from 800 μΩ cm for unprocessed film to 650 μΩ cm after annealing to 1000 °C has been observed.

All Ta–Si–N films listed in Table 1 were tested as diffusion barriers between Au and GaAs.

Fig. 3 shows the sheet resistance changes for various GaAs/Ta–Si–N/Au samples with annealing temperature. The initial sheet resistance of all the as-deposited samples corresponds to the resistivity of highly conductive Au overlayer (the resistivities of both semi-insulating GaAs substrate and Ti–Si–N barrier layer exceeded that of Au film). The resistivity of 90 nm thick Au overlayer was $\rho \approx 4$ μΩ cm, which compares well with bulk resistivity of gold, being 2 μΩ cm [7].

Here, for comparison purposes, the behaviour of pure Au metallisation in direct contact with GaAs is shown. Low temperature Au-Ga eutectic (340 °C [7]) and resultant Au-GaAs interaction explains the increase of resistivity after 400 °C annealing [7,8].

As for Ta–Si–N barrier layers, first annealing steps at 400 and 500 °C caused the decrease of R_s by approximately 30% for GaAs/$Ta_{67}Si_{33}$/Au and GaAs/Ta–Si–N/Au samples. As this reduction is not due to metallurgical or chemical reactions, it may be explained by thermally activated grain size growth in the gold layer.

For GaAs/$Ta_{67}Si_{33}$/Au samples, R_s values remain nearly unchanged up to annealing temperature of 500 °C. An increase of sheet resistance after annealing at 600 °C indicates, that nitrogen-free Ta–Si barrier failed. In contrast, for all GaAs/Ta–Si–N/Au samples, the sheet resistance remains nearly unchanged up to annealing temperature of 700 °C (Fig. 3). Ta–Si–N films with nitrogen concentration from 27 to 36% prevent interactions between Au and GaAs temperatures up to 700 °C (failure temperature ≈800 °C).

Fig. 4a shows backscattering spectra for the GaAs/$Ta_{53}Si_{20}N_{27}$/Au sample before and after annealing at 800 °C. It is obvious that this barrier fails as a result of annealing. In contrast, $Ta_{34}Si_{25}N_{41}$ exhibits excellent diffusion barrier properties. The RBS spectra for as-deposited and annealed at 800 °C samples overlap (Fig. 4b), indicating that the intermediate amorphous $Ta_{34}Si_{25}N_{41}$ film totally prevented the interaction between Au and GaAs.

4. Conclusion

Amorphous Ta–Si and Ta–Si–N thin films of various compositions were deposited by reactive r.f. magnetron sputtering from Ta_5Si_3 target and tested as diffusion barriers for Au metallisation on GaAs substrate. It has been demonstrated that electrical resistivity and crystallisation temperature increase with increasing nitrogen content in the films. Amorphous $Ta_{67}Si_{33}$ films crystallise at 600 °C into Ta_5Si_3 and $TaSi_2$ phases. As for the most stable ternary $Ta_{34}Si_{25}N_{41}$ films, crystallisation starts at above 900 °C and leads to formation of two distinct phases: Ta_5Si_3 and $TaN_{0.8}$.

Binary $Ta_{67}Si_{33}$ film, as a diffusion barrier between GaAs substrate and Au, does not degrade up to 500 °C. Failure takes place approximately 600 °C and is the most probably initiated by the crystallisation of the Ta–Si material. Ta–Si–N films formed much more effective diffusion barriers. A 100 nm thick $Ta_{34}Si_{25}N_{41}$ film showed excellent barrier property and prevented the interaction between Au and GaAs after annealing at 800 °C.

Acknowledgments

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