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# DIFFUSION BARRIER PROPERTIES OF REACTIVELY SPUTTERED W-Ti-N THIN FILMS

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**Abstract.** Thin W-Ti-N films were deposited by reactive d.c. magnetron sputtering from a W-Ti (30 at.%) target in Ar-$N_2$ gas mixture and tested as diffusion barrier between GaAs and Au. The films were investigated by four-point probe sheet resistance measurements, profilometry, Rutherford backscattering spectrometry, X-ray diffraction and atomic force microscopy. The physical and diffusion barrier properties of sputter-deposited W-Ti-N depend on the concentration of nitrogen in the films. We found that the film growth rate decreases with increasing ratio of the nitrogen partial pressure, while the resistivity and nitrogen content in the films increases. The $W_{78}Ti_{22}$ structure is β-W matrix seeded with fine α-Ti precipitates. For $W_{65}Ti_{17}N_{18}$ films, the structure is a dense mixture of ultrafine crystallites of tungsten, TiN, $W_2N$ and/or $Ti_2N$ and amorphous phase. At high nitrogen concentrations N > 30 at.%, the structure is a mixed phase of $W_2N$ and TiN. The improved barrier performance of the films with additional nitrogen was due to the 'stuffing' of the grain boundaries with nitrogen. The most thermally stable $W_{65}Ti_{17}N_{18}$ thin films prevent interaction between Au and GaAs up to 750 °C.

## 1. INTRODUCTION

The fabrication of thermally stable contact metallization is essential for successful device performance. In the case of contact to III-V semiconductors the Au-based metallization is still attractive because gold has low resistivity, superior electromigration resistance and chemical inertness. These metallizations, however, are known to fail at temperatures between 400 and 500 °C [1,2] because the semiconductor reacts with the gold overlayer. Therefore, the development of an effective barrier material against interfacial reaction between Au-overlayer and semiconductor substrate is essential for the realization of Au-based metallization to III-V semiconductors.

The exceptional combination of properties of transition metal nitrides such as high electrical conductivity, thermal and chemical resistance makes these materials useful for diffusion barriers in contact systems to semiconductor devices [3-6].

In this work, we investigate the deposition process, properties and diffusion barrier performance of W-Ti-N thin films between Au and GaAs. This study was focused on the effect of the nitrogen content in W-Ti-N thin films on the physical properties and the diffusion barrier performance.

## 2. EXPERIMENTAL

The W-Ti-N films were deposited by reactive magnetron sputtering from a W-Ti (30 at.%) target (15

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**Table 1.** Properties of reactively sputtered W-Ti-N films obtained at various $N_2$ partial pressures.

| Film composition (at.%) | Nitrogen pressure (Pa) | Argon pressure (Pa) | Deposition rate (nm/min) | Electrical resistivity ($10^{-3}$ Ωcm) | Average grain size (nm) | RMS-roughness (nm) |
|---|---|---|---|---|---|---|
| $W_{78}Ti_{22}$ | 0 | 0.50 | 88.0 | 0.106 | 31 | 1.75 |
| $W_{65}Ti_{17}N_{18}$ | 0.02 | 0.48 | 85.5 | 0.243 | 32 | 1.10 |
| $W_{56}Ti_{14}N_{30}$ | 0.05 | 0.45 | 73.0 | 0.300 | 34 | 2.25 |
| $W_{40}Ti_{11}N_{49}$ | 0.25 | 0.25 | 47.0 | 0.464 | 23 | 1.15 |
| $W_{36}Ti_{11}N_{53}$ | 0.30 | 0.20 | 41.0 | 0.650 | 21 | 1.43 |
| $W_{34}Ti_{11}N_{55}$ | 0.35 | 0.15 | 32.5 | 0.845 | 12 | 1.17 |

cm in diameter) in Ar-$N_2$ gas mixture. The target-to-substrate distance was about 7 cm. A d.c. power density of 1.7 W/cm$^2$ was applied to the target and the partial pressure of $N_2$ was varied from 0 to 0.35 Pa at a total gas pressure of 0.5 Pa. Prior to deposition the vacuum pressure was about $1 \cdot 10^{-4}$ Pa. The target was given a 1 min sputter clean against a shutter at 2 W/cm$^2$ before each deposition.

The substrates were semi-conducting GaAs (100) wafers. Prior to loading into the sputtering chamber, the wafers were cleaned in organic solvents (trichloroethylene, acetone, methanol), and etched in $NH_4OH:H_2O_2:H_2O = 20:7:973$ ($t = 2$ min), rinsed in de-ionised $H_2O$ ($t$ = 2 min), dipping in $NH_4OH:H_2O = 1:10$ ($t = 15$ s), and blown dry with $N_2$.

The film thickness was measured by α-step profilometer and film resistivity was calculated from the sheet resistance ($R_s$) measured by a four-point probe. The phases and chemical composition of W-Ti-N films have been investigated by X-ray diffraction method (XRD) and Rutherford backscattering spectrometry (RBS). For determination of the composition of W-Ti-N films by RBS, carbon substrates were used to reduce the background in the nitrogen signal. Surface morphology, grain size and root-mean square (RMS) roughness were examined using atomic force microscopy (AFM).

To determine the diffusion barrier performance of the W-Ti-N films in the GaAs/barrier/Au system, a gold overlayer (200 nm) was deposited in the d.c. mode in pure Ar at a gas pressure of 0.5 Pa and a sputtering power density of 1.6 W/cm$^2$ on the 100 nm thin barrier films. After annealing for 5 min up to 800 °C in Ar ambient the samples were characterized with RBS and sheet resistance measurements.

## 3. RESULTS AND DISCUSSION

The influence of $N_2$ partial pressure ($p_{N2}$) on the film properties is shown in Table 1. The N content in the films increases with the $N_2$ partial pressure and tends to saturation when the $p_{N2}$ exceeds 0.2 Pa, because a greater number of reactive nitrogen incorporate into the film during the sputtering process. The increase in N concentration may also be related to the drop in sputtering rate with increasing $N_2$ partial pressure, because nitrogen had more time to react and to be incorporated into the film. For films reactively sputtered at $p_{N2} = 0.25$ Pa, the growth rate is only about 50% of that in pure Ar. At the same time the N concentration in the films increases steeply at first and then tends to saturate at about 50 at.%. The decrease in the deposition rate results partly from the lower efficiency of the nitrogen atoms with regard to argon atoms and partly from the target poisoning effects where the sputtering yield for nitride is much smaller than the metal. Between the values of $p_{N2}$ = 0.02–0.05 Pa, the deposition rate drops more steeply, which is indicative of changes in the sputtering mode (transition from a metallic to a nitride target), as well as in the film structure (from amorphous to polycrystalline films). Similar trends in nitrogen concentration and deposition rate have been reported previously [7,8], but the functional dependences on the $N_2$ partial pressure of those results and ours cannot readily be compared because the $p_{N2}$ was varied under different experimental conditions.

Our XRD measurements indicate that the crystallographic structure of sputter-deposited W-Ti-N depends on the concentration of nitrogen in the films. The XRD analyses reveal that the film deposited in pure Ar consists of a β-W matrix seeded with fine α-Ti precipitates. A broadened X-ray diffraction peak is observed in W-Ti-N film deposited at $p_{N2}$ = 0.02

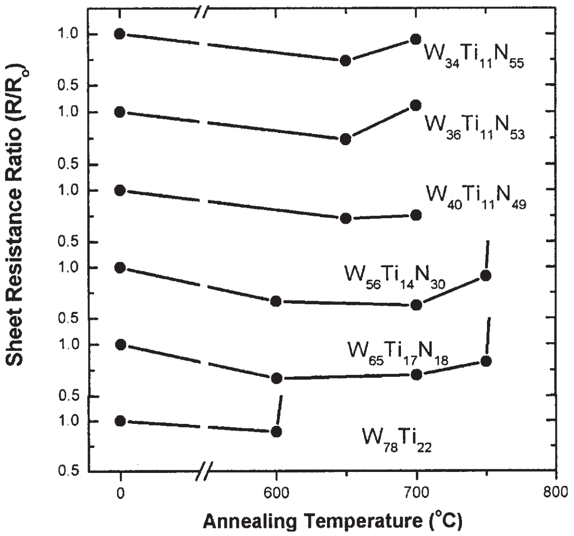

**Fig. 1.** Normalized sheet resistance of GaAs/W-Ti-N/Au samples as a function of the annealing temperature.

Pa, indicating in complex character of the phase changes which occur when the nitrogen content of the films increases. Ternary $W_{65}Ti_{17}N_{18}$ films may be described as a dense mixture of ultrafine crystallites of tungsten, TiN, $W_2N$ and/or $Ti_2N$ and amorphous phase. At high nitrogen concentrations N > 30 at.%, a single f.c.c. phase was observed. This crystal structure could be interpreted in terms of a mixed phase (solid solution) $W_2N$/TiN ($W_{1-y-x}Ti_xN_y$). Such changes in the W-Ti-N film structure were also described by Shaginyan *et al.* [7], Dirks *et al.* [8,9], Cavaleiro *et al.* [10], and Oparowski *et al.* [11].

The AFM measurement was used to study the variation of grain size and root-mean square (RMS) roughness as a function of the $N_2$ partial pressure. The grain size increases with the $p_{N2}$ in the range from 0 to 0.05 Pa and decreases for $p_{N2} > 0.05$ Pa. Concerning the RMS roughness, its value increases from $p_{N2} = 0.02$ Pa and reaches 2.25 nm for $p_{N2} = 0.05$ Pa and decreases for $p_{N2} = 0.25$ Pa and stays approximately equal to 1.2 nm up to $p_{N2} = 0.35$ Pa.

Resistivity of as-deposited W-Ti-N thin films depended on their composition and structure. The resistivity of pure $W_{78}Ti_{22}$ film was $0.1\cdot10^{-3}$ Ωcm and rose slowly up to $0.3\cdot10^{-3}$ Ωcm for the ternary $W_{56}Ti_{14}N_{30}$ film. When the nitrogen content reached more than 30 at.%, the film resistivity started to increase steeply , which may be attributed to the reduction in grain size: 23 nm for $W_{40}Ti_{11}N_{49}$ ($0.464\cdot10^{-3}$ Ωcm), and 12 nm for $W_{34}Ti_{11}N_{55}$ ($0.845\cdot10^{-3}$ Ωcm).

To evaluate the diffusion barrier performance of W-Ti-N films, GaAs/barrier/Au samples were annealed at various temperatures and analysed by RBS and $R_s$ measurement. Fig. 1 shows the sheets resistance of annealed samples, normalized to the as-deposited value. The stability of the sheet resistance of a metallization system is an important property and an indicator of metallurgical and chemical interactions [12]. The initial sheet resistance ($R_o \approx 0.2$ Ω/sq.) of all the as-deposited samples corresponds to the Au resistivity of about $4\cdot10^{-6}$ Ωcm, which compares well with bulk resistivity of gold of about $2\cdot10^{-6}$ Ωcm. The first annealing step at 600 °C decreases $R_s$ by about 10% for GaAs/W-Ti/Au and 30% for GaAs/W-Ti-N/Au samples due to the grain growth of Au overlayer. However, the decrease of $R_s$ only a 10% at 600 °C of GaAs/$W_{78}Ti_{22}$/Au samples may be explained by start to failure of diffusion barrier, and abrupt increase of $R_s$ at 700 °C indicates a catastrophic failure, which is confirmed by RBS analysis (Fig. 2a). For GaAs/$W_{65}Ti_{17}N_{18}$/Au sample, the sheet resistance remains nearly unchanged up to annealing temperature of 750 °C and increase drastically upon annealing at 800 °C, indicating a significant failure of the diffusion barrier (Fig. 1). The RBS spectra of as-deposited and annealed at 750 °C samples overlap (Fig. 2b), indicating that intermediate a $W_{65}Ti_{17}N_{18}$ barrier prevents the interaction between Au and GaAs. It is obvious that this barrier fails as a result of annealing at 800 °C. The sheet resistance values, as well as the backscattering spectra (Fig. 2c and 3a), of GaAs/$W_{56}Ti_{14}N_{30}$/Au and GaAs/$W_{40}Ti_{11}N_{49}$/Au samples remain unchanged up to annealing at 700 °C, indicating that any detectable interaction between Au and the barriers does not take place. The sheet resistance of the GaAs/$W_{56}Ti_{14}N_{30}$/Au sample started to increase gradually at 750 °C before an abrupt increase at 800 °C as shown in Fig. 1. The RBS spectra of the annealed samples show an interfacial interaction between Au and barrier after heat-treatment. Both sheet resistance and backscattering measurements show thermal stability at 650 °C (Fig. 1 and 3b,c) for GaAs/$W_{36}Ti_{11}N_{53}$/Au and GaAs/$W_{34}Ti_{11}N_{55}$/Au samples. At 700 °C, the sheet resistance increase, indicating a failure of the diffusion barriers and interfacial interaction are observed in the RBS spectra. As shown in Fig. 3, interdiffusion in GaAs/barrier/Au structure increases with the decrease of barrier films grains size of some similar compositions during thermal annealing. It is motivated by the fact that decreasing of grain size leads to increasing of density of

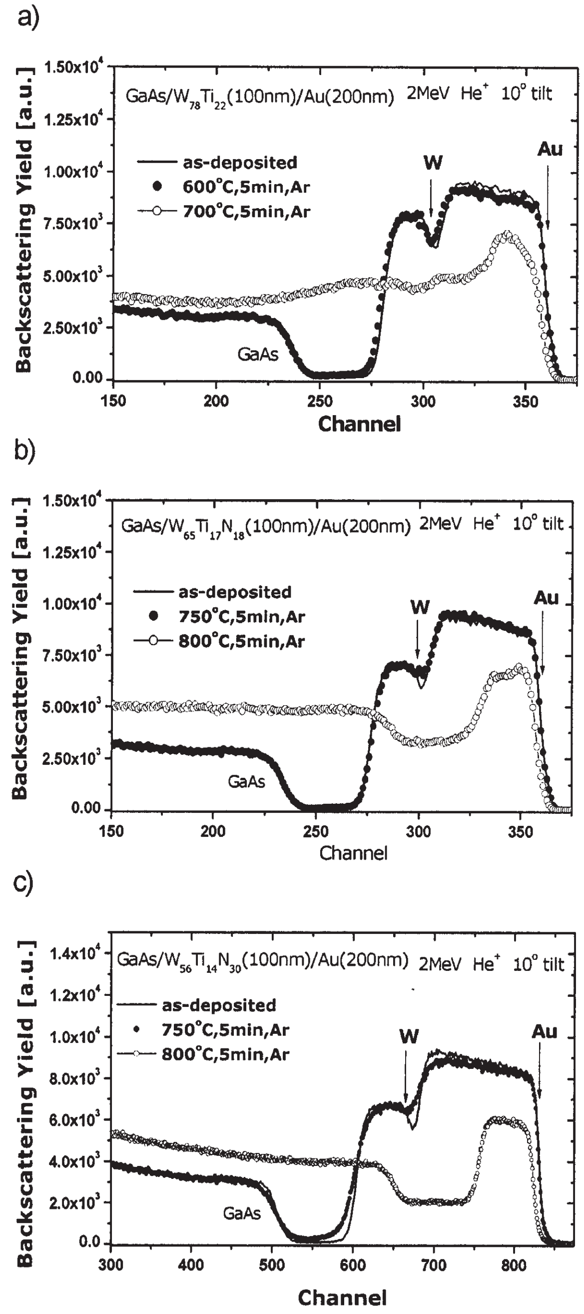

**Fig. 2.** RBS spectra of samples before and after annealing in Ar at 800 °C for 5 min: (a) GaAs/$W_{78}Ti_{22}$/Au; (b) GaAs/$W_{65}Ti_{17}N_{18}$/Au; (c) GaAs/$W_{56}Ti_{14}N_{30}$/Au.

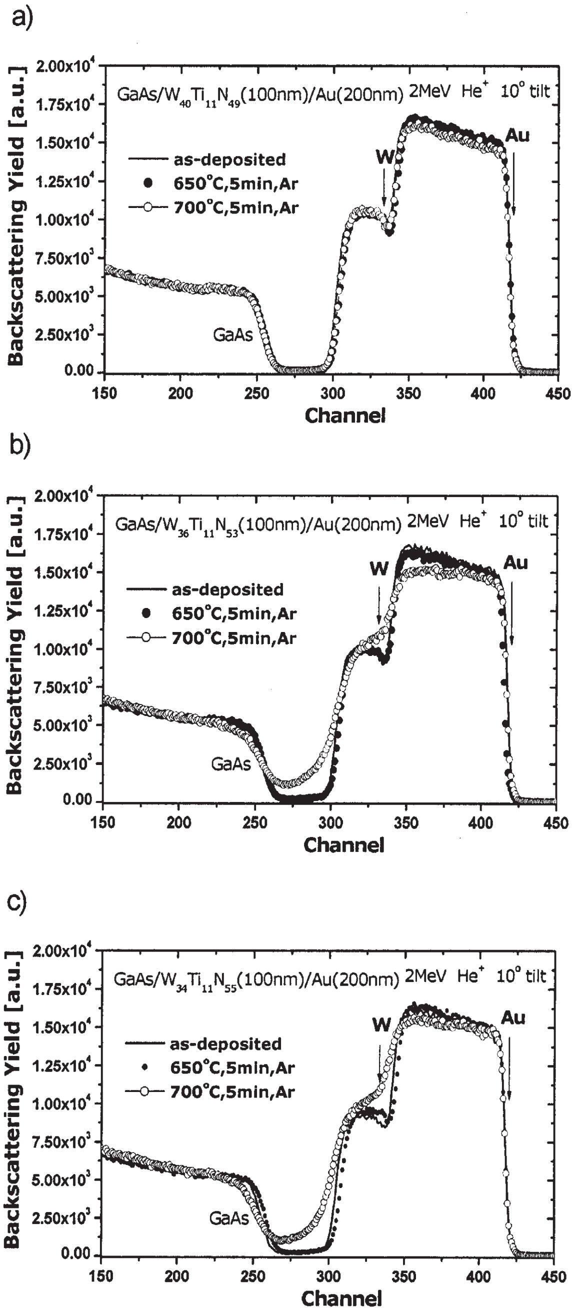

**Fig. 3.** RBS spectra of samples before and after annealing in Ar at 800 °C for 5 min: (a) GaAs/$W_{40}Ti_{11}N_{49}$/Au; (b) GaAs/$W_{36}Ti_{11}N_{53}$/Au; (c) GaAs/$W_{34}Ti_{11}N_{55}$/Au.

grain boundaries along which the diffusion process mainly occur. For GaAs/$W_{40}Ti_{11}N_{49}$/Au, GaAs/$W_{36}Ti_{11}N_{53}$/Au and GaAs/$W_{34}Ti_{11}N_{55}$/Au samples, the Au overlayer disappeared after annealing at 750 °C that caused by the full diffusion of gold in site the sample.

## 4. CONCLUSION

The investigation of W-Ti-N thin films, deposited by reactive d.c. magnetron sputtering showed that the structure, composition, resistivity and diffusion barrier performance are strongly dependent on the nitrogen concentration in the films.

A ternary $W_{65}Ti_{17}N_{18}$ barrier deposited at $p_{N2}$ = 0.02 Pa was shown to be most effective in retarding the interdiffusion of Au and GaAs. Thermal annealing of GaAs/barrier/Au structures with these films showed excellent barrier properties up to 750 °C. The crystal structure of this film was determined to be a dense mixture of ultrafine crystallites of tungsten, TiN, $W_2N$ and/or $Ti_2N$ and amorphous phase. This complexity of the structure (amorphous + nanocrystalline), results in a substantial improvement in the barrier properties of these films compared with polycrystalline W-Ti-N films. In general, the improved barrier properties of W-Ti-N films by the incorporation of nitrogen may be explained in terms of 'stuffing the grain boundaries with nitrogen'.

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