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

A.V. Kuchuk1, V.P. Kladko1, V.F. Machulin1, A. Piotrowska2, E. Kaminska2, K. Golaszewska2, R. Ratajczak3 and R. Minikayev4

1V. Lashkaryov Institute of Semiconductor Physics NASU, pr. Nauki 45, 03028 Kiev, Ukraine
2Institute of Electron Technology, Al. Lotnikow 32/46, 02-668 Warsaw, Poland
3The Andrzej Soltan Institute for Nuclear Studies, Hoza str. 69, 00-681 Warsaw, Poland
4Institute of Physics PAS, Al. Lotnikow 32/46, 02-668 Warsaw, Poland

Received: October 26, 2004

Abstract. Thin W-Ti-N films were deposited by reactive d. c. magnetron sputtering from a W-Ti (30 at.%) target in Ar-N2 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 W0.35Ti0.65 structure is β-W matrix seeded with fine α-Ti precipitates. For W0.35Ti0.65N films, the structure is a dense mixture of ultrafine crystallites of tungsten, TiN, W2N and/or Ti3N4 and amorphous phase. At high nitrogen concentrations N > 30 at.%, the structure is a mixed phase of W2N 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 W0.35Ti0.65N 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
cm in diameter) in Ar-N₂ gas mixture. The target-to-substrate distance was about 7 cm. A d.c. power density of 1.7 W/cm² was applied to the target and the partial pressure of N₂ 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 1·10⁻⁴ Pa. The target was given a 1 min sputter clean against a shutter at 2 W/cm² 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 NH₂OH·H₂O₂·H₂O = 20:7:973 (t = 2 min), rinsed in de-ionised H₂O (t = 2 min), dipping in NH₂OH·H₂O = 1:10 (t = 15 s), and blown dry with N₂.

The film thickness was measured by ɑ-step profilometer and film resistivity was calculated from the sheet resistance (Rₛ) 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/cm² 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 N₂ partial pressure (pₙ₂) on the film properties is shown in Table 1. The N content in the films increases with the N₂ partial pressure and tends to saturation when the pₙ₂ 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 N₂ partial pressure, because nitrogen had more time to react and be incorporated into the film. For films reactively sputtered at pₙ₂ = 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 pₙ₂ = 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 N₂ partial pressure of those results and ours cannot readily be compared because the pₙ₂ 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 pₙ₂ = 0.02

<table>
<thead>
<tr>
<th>Film composition (at.%)</th>
<th>Nitrogen pressure (Pa)</th>
<th>Argon pressure (Pa)</th>
<th>Deposition rate (nm/min)</th>
<th>Electrical resistivity (10⁻³ Ωcm)</th>
<th>Average grain size (nm)</th>
<th>RMS-roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WₓTiᵧ</td>
<td>0.02</td>
<td>0.48</td>
<td>85.5</td>
<td>0.243</td>
<td>32</td>
<td>1.10</td>
</tr>
<tr>
<td>WₓTiᵧNₐ</td>
<td>0.25</td>
<td>0.25</td>
<td>73.0</td>
<td>0.300</td>
<td>34</td>
<td>2.25</td>
</tr>
<tr>
<td>WₓTiᵧNₐ</td>
<td>0.30</td>
<td>0.20</td>
<td>47.0</td>
<td>0.464</td>
<td>23</td>
<td>1.15</td>
</tr>
<tr>
<td>WₓTiᵧNₐ</td>
<td>0.35</td>
<td>0.15</td>
<td>42.0</td>
<td>0.850</td>
<td>21</td>
<td>1.43</td>
</tr>
<tr>
<td>WₓTiᵧNₐ</td>
<td>0.45</td>
<td>0.15</td>
<td>32.5</td>
<td>0.845</td>
<td>12</td>
<td>1.17</td>
</tr>
</tbody>
</table>
Pa, indicating in complex character of the phase changes which occur when the nitrogen content of the films increases. Ternary W_{55}Ti_{45}N_{10} films may be described as a dense mixture of ultrafine crystallites of tungsten, TiN, W_{2}N and/or Ti_{2}N 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_{x}N/TiN (W_{1+y}Ti_{1-x}N). 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_{N_{2}} in the range from 0 to 0.05 Pa and decreases for p_{N_{2}} > 0.05 Pa. Concerning the RMS roughness, its value increases from p_{N_{2}} = 0.02 Pa and reaches 2.25 nm for p_{N_{2}} = 0.05 Pa and decreases for p_{N_{2}} = 0.25 Pa and stays approximately equal to 1.2 nm up to p_{N_{2}} = 0.35 Pa.

Resistance of as-deposited W-Ti-N thin films depend on their composition and structure. The resistivity of pure W_{78}Ti_{22} film was 0.1-10^{3} Ωcm and rose slowly up to 0.3-10^{3} Ωcm for the ternary W_{55}Ti_{45}N_{10} 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} (0.464·10^{3} Ωcm), and 12 nm for W_{38}Ti_{12}N_{50} (0.845·10^{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_{f} 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_{f} ≈ 0.2 Ω/sq.) of all the as-deposited samples corresponds to the Au resistivity of about 4·10^{-6} Ωcm, which compares well with bulk resistivity of gold of about 2·10^{-6} Ωcm. The first annealing step at 600 °C decreases R_{f} 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_{f} only at 600 °C of GaAs/W_{55},Ti_{45}N_{10}/Au samples may be explained by start to failure of diffusion barrier, and abrupt increase of R_{f} at 700 °C indicates a catastrophic failure, which is confirmed by RBS analysis (Fig. 2a). For GaAs/W_{55},Ti_{45}N_{10}/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_{55},Ti_{45}N_{10}/Au 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_{55},Ti_{45}N_{10}/Au and GaAs/W_{50},Ti_{10}N_{40}/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_{55},Ti_{45}N_{10}/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_{55},Ti_{45}N_{10}/Au and GaAs/W_{50},Ti_{10}N_{40}/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_{30}Ti_{13}Au; (b) GaAs/W_{30}Ti_{13}N_{40}/Au; (c) GaAs/W_{30}Ti_{13}N_{40}/Au.

Fig. 3. RBS spectra of samples before and after annealing in Ar at 800 °C for 5 min: (a) GaAs/W_{30}Ti_{13}N_{40}/Au; (b) GaAs/W_{30}Ti_{13}N_{40}/Au; (c) GaAs/W_{30}Ti_{13}N_{40}/Au.

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_{30}Ti_{13}N_{40} barrier deposited at p_{c}=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, W2N and/or Ti2N 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’.

REFERENCES