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INVESTIGATION OF THE INTERFACE INTEGRITY OF THE THERMALLY STABLE WN/GaAs SCHOTTKY CONTACTS

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ABSTRACT

WN_x/GaAs Schottky contacts formed by reactive sputtering were found to be thermally stable up to an annealing temprature of ~900 °C. The interface morphology and structure of this contact under high temperature annealing conditions (> 700 °C) have been investigated by transmission electron microscopy (TEM) and x-ray diffractometry techniques. For the as-deposited samples, the thin film had an amorphous structure. After annealing at high temperatures, the amorphous phase transformed to α-W and W_2N phases. However, the contact interface remained thermally stable up to 850 °C. Cross-sectional TEM micrographs revealed that annealing at temperatures above 850 °C resulted in the formation of 'pockets' beneath the interface. This phenomenon has been correlated with the electrical properties of the contacts, e. g., an enhancement of the barrier height of the contact. Comparisons between the interface morphology of this system and other refractory metal nitride contacts (e. g., TiN/GaAs) are also presented.

INTRODUCTION

One of the most important processing steps in the fabrication of GaAs MESFET's using the self-aligned technique involves ≥800 °C post-implant annealing to activate the implanted dopants in the GaAs substrate after the formation of the gate contact. A number of investigations have shown that refractory metal silicides and nitrides are excellent candidates for the thermally stable gate metals needed in the self-aligned technology due to their high thermodynamic stability and low resistivity [1]. Recently, the study by Zhang et al. [2] showed that the refractory metal nitrides (NbN, TiN and ZrN) used as Schottky gate metals are very promising not only because of their high thermal stability and low resistivity, but also because of their improved electrical characteristics after annealing at high temperatures up to 900 °C. Tungsten (W), its silicide (WSi_x) and nitride (WN_x) have also received attentions from researchers. This is especially true for tungsten nitride (WN_x), since WN_x has lower resistivity than tungsten silicide, and can be formed easily by reactive sputtering from a pure W target in Ar/N_2 atmosphere. Yu et al. [3] recently reported a systematic study on the structural and electrical characteristics of WN_x/GaAs contacts under various annealing conditions, e. g., different nitrogen content in the films, annealed with or without a capping layer, and annealed in As overpressure and a flowing N_2 ambient.

In this study, TEM and x-ray diffractometry (XRD) were used to investigate the interface structure and morphology of the WN_x/GaAs contacts. The results of this structural study are correlated with the electrical characteristics.

EXPERIMENTS

Undoped and Si-doped ($N_D = 1.5 \times 10^{17} cm^{-3}$) GaAs wafers with (100) orientation were prepared for WN_x deposition by degreasing in organic solvants, etching in $HCl:H_2O$ solution, rinsing in de-ionized water and drying with nitrogen gas. Prior to loading into the deposition champer, the wafers were dipped in a $NH_4OH:H_2O$ solution for 1 min. for removal of the native oxide from the GaAs surface. The WN_x films (~200 nm) then were deposited on the GaAs substrates by reactive dc sputtering. The total gas pressure was kept at 10 mTorr during the deposition. The relative partial pressure of nitrogen was used to control nitrogen content in the as-deposited WN_x films. In this work, the partial pressure of nitrogen was 20%.

The WN_x samples were annealed under different conditions. A set of samples were capped with an SiO_2 layer (~100 nm) by chemical vapor deposition. The samples were then furnace annealed (FA) at 700-850 °C for 30 min. under an As-overpressure or in flowing N_2. Some of the capped samples were annealed at 850, 900 and 950 °C for 10 seconds in a flowing Ar ambient in a halogen lamp rapid thermal annealing (RTA) system.

Cross-sectional samples were prepared by the standard techniques for TEM investigations [4]. The study of the interface structure and morphology of the WN_x/GaAs contacts before and after RTA was performed in a Philips EM400 TEM and a JEOL 200CX TEM. A Siemens D500 x-ray diffractometer was also used to characterize the structure of the samples before and after annealing, and to confirm the TEM results on a macroscopic scale.

RESULTS AND DISCUSSIONS

The interface morphology and structure of the WN_x/GaAs contacts have been studied by TEM. Figure 1 shows the TEM images of cross-sectional samples before and after RTA at 850 °C, 900 °C and 950 °C. For the as-deposited sample, the interface was relatively flat and no native oxide was observed. The structure of the as-deposited WN_x thin film with 20% N_2 was studied by the selected area diffraction technique. Figure 2a shows a selected area diffraction pattern for this as-deposited sample in which a β-W amorphous ring pattern is superimposed on the [110] GaAs diffraction pattern. Since this diffraction pattern was taken from the interface area where the amorphous film had a thickness of only ~15 nm, only the strongest 210 reflection from the β-W amorphous film is visible. β-W has a cubic structure with a lattice parameter $a_o = 0.5050$ nm.

The interface morphology of the sample after RTA at 850 °C is shown in Fig. 1b. The interface in this case was not flat, and there was some evidence that interface interdiffusion occured during annealing. It is likely that some of the Ga and As atoms diffused into the WN_x film locally, and some As atoms may have diffused out along the grain boundaries in the film. RTA at 850 °C resulted in a crystallization of the as-deposited amorphous film. The crystallized grains in the film have been identified to be α-W and W_2N by XRD and electron diffraction techniques. As can be seen in Fig. 2b, a $[\bar{1}11]$ α-W diffraction pattern from one α-W single grain is superimposed on the [110] GaAs diffraction pattern. Note also that 110 α-W diffraction spots from another α-W grain shown on the left of the diffraction pattern are only a few degrees from the 111 diffraction spots of W_2N. This may indicate an epitaxial relationship between this α-W single grain and the W_2N grain since the lattice mismatch between the 110 α-W d-spacing (0.2238 nm) and the 111 W_2N d-spacing (0.2382 nm) is only 6.2%. Both α-W and W_2N have a cubic structure with lattice parameters 0.3165 nm and 0.4126 nm, respectively. From the x-ray and electron diffraction analysis, the majority phase in the film was α-W with a smaller amount of W_2N (20% of W_2N reported by Yu et al. [3]).

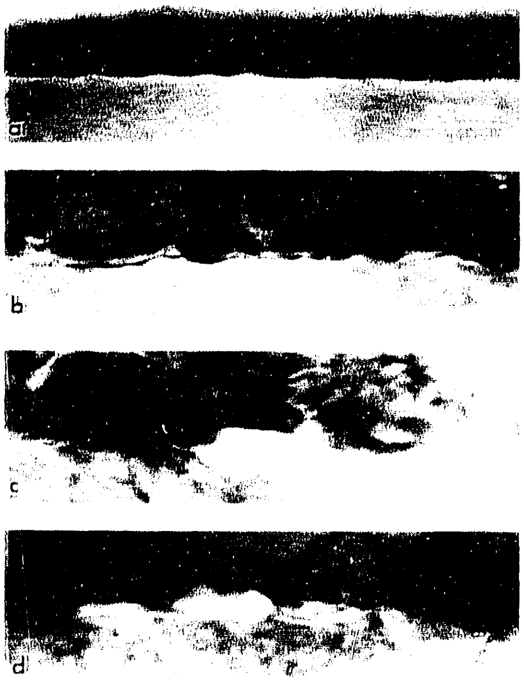

Fig.1. Transmission electron microscopy images of cross-sectional WN_x/GaAs samples (a) as-deposited, (b) after RTA at 850 °C, (c) RTA at 900 °C, and (d) RTA at 950 °C.

After RTA at 900 °C, the interface of the WN_x/GaAs contacts became very rough with pocket-like protrusions formed under the original interface of the WN_x/GaAs contact as shown in Fig. 1c. These pockets have an amorphous-like appearance as has been observed for TiN/GaAs contacts after annealing at temperatures above 800 °C [5]. The average width of the pockets is ~15 nm, and the average penetration depth of the pockets into the substrate is about 10 nm. It is expected that some W_2As_3 phase may be formed on the top of the pockets by outdiffusion of As atoms from the substrate. However, electron and x-ray diffraction results do not show any W_2As_3 patterns. This may be due to the very small amount of this phase present in the film.

RTA at 950 °C resulted in a very rough interface as shown in Fig. 1d. As shown in this figure, many more pocket-like protrusions were formed as compared with 900 °C RTA so that there is now no spacing left between them. This indicates that a significant interface interdiffusion has occured during the 950 °C RTA. By measuring the lattice spacings from the phase at the top of these pockets in Fig. 1d, it was clear that the phase in intimate contact with GaAs was W_2N since only two phases, α-W and W_2N, were present in the thin film as indicated by electron and x-ray diffraction analysis. It is likely that both Ga and As atoms diffused along the grain boundaries in the thin film to the surface since diffusion in grain boundaries is much faster than in the bulk. Outdiffusion of Ga and As atoms apparently requires an annealing temperatures above 850 °C because the first appearence of pockets beneath the original interface was after 900 °C RTA.

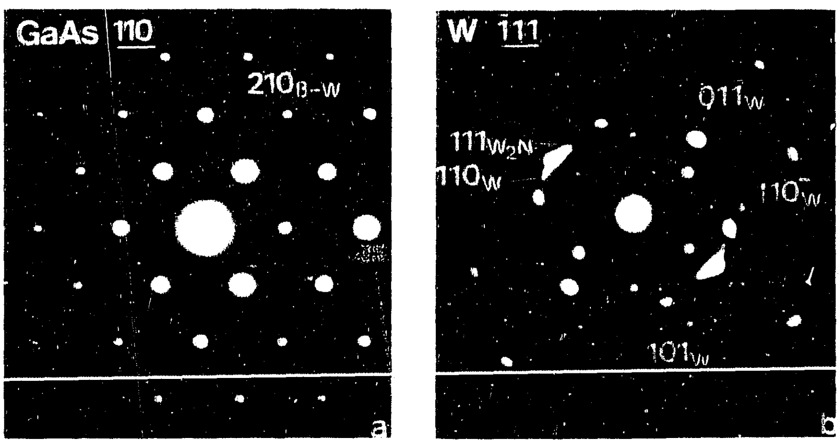

Fig.2. Electron diffraction patterns from (a) the as-deposited sample, and the sample after RTA at 850 °C.

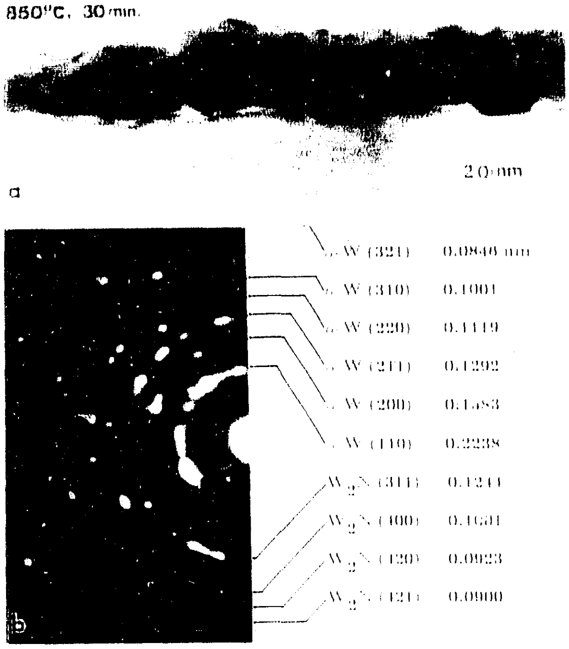

Fig.3. (a) TEM image of the capped WN_x/GaAs sample after FA at 850 °C for 30 min., (b) Electron diffraction pattern from the thin film of the same sample.

For the samples subjected to FA at 850 °C for 30 min. with and without SiO_2 caps, the interface morphology was almost identical with that after 850 °C RTA. This implies that annealing time at 850 °C is not an important variable compared to annealing temperature in determining the interface morphology. Figure 3a shows the interface morphology of the capped WN_x/GaAs sample after annealing at 850 °C for 30 min. From this bright field TEM image, the interface can be seen to be similar to that of 850 °C RTA annealed samples. In some regions the GaAs substrate was consumed by outdiffusion during annealing. The phase in intimate contact with the GaAs was again found to be W_2N by measuring the lattice spacings in Fig. 3a. This confirms the prediction by Yu et al. [3]. Figure 3b shows the selected area diffraction pattern taken from the film only. The rings in this diffraction pattern were found to correspond to α-W and W_2N phases. From the relative intensities of the diffraction rings, α-W was the major phase in the film.

Results from the TEM cross-sectional samples did not show any difference in the interface morphology between the capless samples annealed in an As overpressure and the capped sample in a flowing N_2 ambient after furnace annealing at 850 °C for 30 min. XRD was also used to study the structure of WN_x/GaAs samples before and after annealing under different conditions, e. g., capped or capless, annealing in an As overpressure or a flowing N_2 gas. Figure 4 shows the x-ray spectra from the capped (a) and capless (b) samples after annealing at 850 °C in a flowing N_2 gas and an As overpressure, respectively. The spectrum from the capped sample indicates that the thin film consists of a mixture of phases, α-W and W_2N. Note that the GaAs (200) diffraction

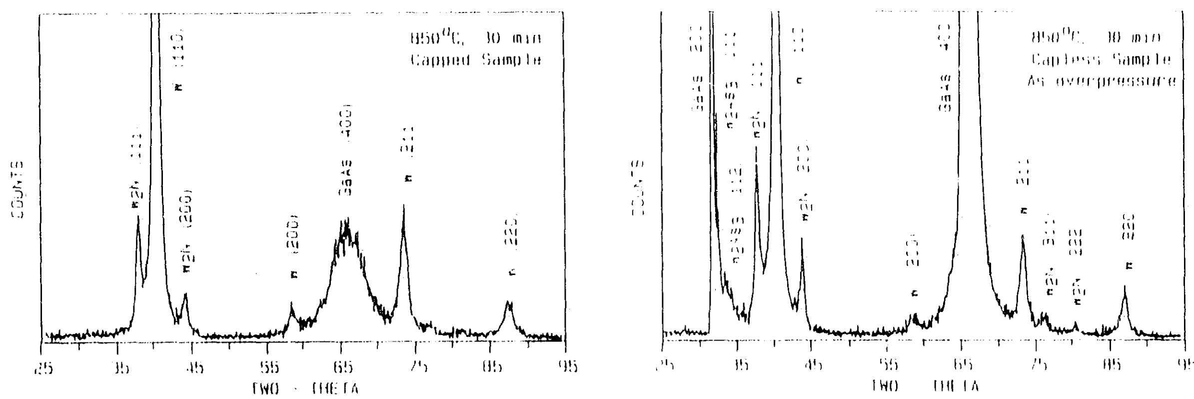

Fig.4. X-ray diffraction spectra of the samples after 850 °C FA for 30 min. (a) capped, and (b) capless.

peak did not appear, and also the GaAs (400) peak has a very low intensity due probably to misorientation of the GaAs substrate from a (100) plane, or the large thickness of the film formed on the GaAs substrate. Compared to the spectrum from the capped sample, the spectrum from the capless sample shows additional peaks corresponding to W_2As_3. Based on a previous Rutherford backscattering spectrometry (RBS) study [3], it is believed that this W_2As_3 phase was formed on the surface of the thin film by the reaction of W on the surface of the film and an As overpressure during annealing. It is also interesting to note that the diffraction intensity of W_2N in the capless sample is higher than that of in the capped sample. This is also in good agreement with the previous RBS study [3].

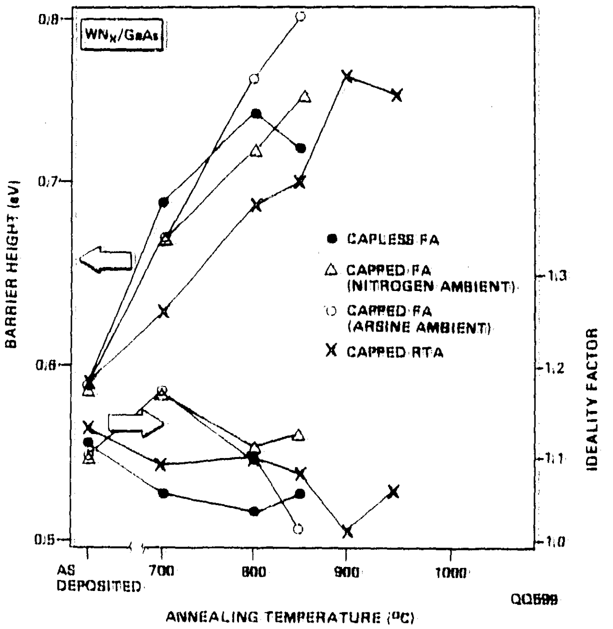

Fig.5. Plots of Φ_b and n as a function of annealing temperature under different annealing conditions for $WN_x/GaAs$ diodes.

Figure 5 shows the electrical characteristics of the $WN_x/GaAs$ contacts before and after annealing in different conditions in the temperature range of 700-850 °C for FA and 700-950 °C for RTA. Yu et al. discussed the effects of nitrogen and annealing conditions on the thermal stability and barrier height of the $WN_x/GaAs$ contacts [3]. The barrier height enhancement with annealing temperatures below 700 °C is attributed to the removal of sputtering damage and consumption of the native oxide at the interface. The reasons for the increase of the barrier height in the nitride contact systems after annealing at temperatures above 700 °C have been a subject of speculation in the literature: (1) the formation of a metal/p^+-GaAs/n-GaAs contact by incorporation of nitrogen into the substrate [2]; (2) the charge states of Ga vacancies formed near the interface [3]; (3) the effective electronegativity of the phase in intimate contact with GaAs [3]. The correct explanation is still not clear.

The results of this investigation show that most of the interface is in intimate contact with W_2N after annealing, and the interface is stable up to 850 °C. It is interesting to note that the pocket-like protrusions were formed above a critical temperature 900 °C RTA as also found for the TiN/GaAs contact where the first appearance of the pockets occurred after 500 °C RTA. The formation of pockets can be explained by outdiffusion of As or Ga and As. This loss of As or Ga and As can change the electronic structure, and create electrically active defects at or near the interface which might result in the barrier height enhancement. For example, it could create a p^+-GaAs thin layer surrounding the pockets [5], or it may change the pinning position of the Fermi-level in the GaAs band gap by loss of As as discussed elsewhere [6].

In summary, the interface morphology and stability of the $WN_x/GaAs$ contacts before and after annealing at high temperatures ($>$ 700 °C) under different conditions have been investigated by TEM and XRD analysis. The as-deposited WN_x film has been found to be β-W with an amorphous structure. Annealing at temperatures up to 850 °C did not change the interface morphology significantly under all annealing conditions, but amorphous β-W transformed to α-W and WN_x phases, with WN_x in intimate contact with the GaAs substrate. Pocket-like protrusions beneath the original interface were observed after RTA at temperatures above 900 °C. Outdiffusion of As or Ga and As along the grain boundaries is considered to be the most likely explanation for the formation of these pockets. These pockets may be partly responsible for the enhancement of barrier height after RTA at temperatures above 850 °C.

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