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Authors
Yu, K.M.
Jaklevic, J.M.
Haller, E.E.

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HIGH TEMPERATURE ANNEALING CHARACTERISTICS OF TUNGSTEN AND TUNGSTEN NITRIDE SCHOTTKY CONTACTS TO GaAs UNDER DIFFERENT ANNEALING CONDITIONS

Kin Man Yu, J. M. Jaklevic, and E. E. Haller
Center for Advanced Materials and Engineering Division, Lawrence Berkeley Laboratory, University of California, Berkeley, Ca 94720.

S. K. Cheung and P. S. Kwok
ABSTRACT

We have investigated systematically the structural and electrical characteristics of thin film tungsten and reactively sputtered tungsten nitride ($WN_x$) Schottky contacts to GaAs under high temperature annealing conditions (with annealing temperatures ranging from 700 to 850°C) in an arsenic-over-pressure and flowing nitrogen ambient with and without silicon dioxide capping layer. Compositions of the $WN_x$ films measured by Rutherford backscattering spectrometry and proton resonant scattering techniques indicate a linear relationship between x and the nitrogen partial pressure during sputtering. Glancing angle X-ray diffraction studies revealed that for non-zero nitrogen partial pressure, the as-deposited films were amorphous, and after annealing these films converted to polycrystalline $W_2N$ and W phases. A surface layer of $W_2As_3$ phase was also observed after As-overpressure capless annealing and was believed to be the result of reactions between W and the ambient As gas. Electrical measurements showed that all $WN_x$/GaAs contacts (with x=0 to 0.5) were thermally stable up to an annealing temperature of 850°C. A diode edge effect is observed for $WN_x$/GaAs diodes cap-annealed in As-overpressure at temperatures higher than 800°C. The maximum achievable Schottky barrier heights for these contacts were found to be independent of the nitrogen content in the films but are influenced by the annealing conditions. We also explored the role played by nitrogen on the thermal stability and barrier height of the contacts.
I. INTRODUCTION

The need for thermally stable GaAs Schottky barriers for the self-aligned gate [1-3] metal-semiconductor field effect transistor (MESFET) technology has stimulated numerous investigations on the interface stability of thin film metal/GaAs contacts under high temperature annealing (≈850°C). Refractory metals, such as tungsten [3-5] and their low resistivity intermetallic compounds, in particular silicides (WSiₓ) [6-9] and nitrides (WNₓ) [10-12] have been shown to form stable Schottky contacts to GaAs even after annealing at 800°C. In addition to thermal stability, for MESFET application, high barrier Schottky contacts are desirable. Recently, Zhang et al [13] reported on a comparative study of refractory metals (Zr, Nb and Ti) and their nitrides as Schottky contacts to n-GaAs. They found that nitride contacts exhibited both improved thermal stability and an enhancement in Schottky barrier heights.

In this paper we report on systematical investigations of the structural and electrical characteristics of tungsten and tungsten nitride (WNₓ) as a function of nitrogen content in the film and whether the structure is annealed with or without a capping layer in an arsenic-overpressure and flowing N₂ ambient. Analytical techniques including Rutherford backscattering spectrometry (RBS), proton resonant scattering (PRS), and x-ray diffraction (XRD) were employed to study the structural properties of the contacts. Diode characteristics of these contacts were studied by current-voltage (I-V) dependence. Film resistivity and stress were also evaluated.
II. EXPERIMENT

Both undoped semi-insulating ($\rho > 10^7 \, \Omega \cdot \text{cm}$) and n-type (Si-doped $N_D = 5 \times 10^{17} \, \text{cm}^{-3}$) GaAs substrates in (100) orientation were degreased in organic solvents and then etched in 1:1 HCl:H$_2$O solution for native oxide removal followed by deionized water rinse and Polyflow dry. The wafers were immersed in an GaAs etching solution to remove mechanical damage on the GaAs surface. Prior to loading into the deposition chamber, the wafers were dipped in an 1:1 NH$_4$OH:H$_2$O solution for one minute. WN$_x$ films were deposited on the GaAs substrates by reactive dc sputtering using a planar magnetron tungsten cathode of 450 cm$^2$ area. A base pressure of 2.5 x 10$^{-7}$ Torr was achieved prior to sputter deposition. A sputtering power of 2kW was used. The total gas pressure, $P$(Ar+N$_2$), was kept at 10mTorr. The relative partial pressure of nitrogen $\gamma$, defined as $\gamma = P(N_2)/P(N_2 + Ar)$, was varied from 0 to 40%.

Capping layers of SiO$_2$ (~1000Å thick) were deposited on some of the samples by chemical vapor deposition at 400°C. 100μm x 100μm diodes of WN$_x$ were fabricated on the n-type GaAs substrates by standard photolithography and reactive-ion-etching in a SF$_6$ plasma. The WN$_x$/GaAs diodes were then furnace annealed (FA) in the range 700 to 850°C for 30 minutes under an arsenic-overpressure or in a flowing N$_2$ ambient. Some of the samples were rapid thermal annealed (RTA) in a flowing Ar ambient using a halogen lamp system in the temperature range of 700 to 950°C for 10 seconds. Ohmic contacts were formed at the back side of the wafer by evaporation of Au-Ge/Ni/Au followed by 2.5 minutes sintering at 390°C in forming gas.

Structural characterization and sheet resistivity measurements of the WN$_x$ films were performed on samples with semi-insulating substrates. A
stylus instrument was used to measure the thickness of the films while a four-point-probe was used to measure their sheet resistance. The film stress was determined from a stress gauge that compared the deflection of a GaAs substrate before and after the film deposition.

Compositions of the films were analyzed with Rutherford backscattering spectrometry and the proton resonant scattering techniques. The RBS experiments were carried out using a 2.0 MeV \(^4\text{He}^+\) beam. The \(^{14}\text{N}(p,p)^{14}\text{N}\) resonance at a proton energy of 1.675 MeV was used in the PRS measurements [14]. The RBS and PRS experiments were carried out with a scattering angle \(\theta = 165^\circ\). The structures of the WN\(_x\) films were characterized by x-ray diffraction in the Seeman-Bohlin geometry with x-ray incident angle \(\theta = 6^\circ\).

Current-voltage (I-V) measurements were used to characterize the WN\(_x\)/GaAs diodes. The Schottky barrier heights of the diodes were obtained by considering the ideal thermionic emission equation:

\[
J = A^* T^2 \exp \left[ \frac{-q\phi_b}{kT} \right] \left[ \exp \left( \frac{qV_a}{nkT} \right) - 1 \right]
\]

where \(J\) is the current density, \(A^*\) is the effective Richardson constant and is equal to 8.16 A/cm\(^2\)/K\(^2\) for GaAs, \(T\) is the measurement temperature, \(k\) is the Boltzmann constant, \(V_a\) is the applied voltage, \(\phi_b\) is the Schottky barrier height of the diode, and \(n\) is the ideality factor which is \(=1.0\) if the thermionic emission process is the dominating current transport mechanism.
III. RESULTS

1. Composition Analysis: RBS and PRS results

Figure 1 and 2 show typical RBS and PRS spectra for WN$_x$/GaAs samples as-deposited and after annealing at 800°C in an As-overpressure. Note the formation of a layer of W-As phase on top of the film as a result of thermally activated reactions between W and the As gas at elevated temperatures. Nominal composition of this W-As phase as measured by RBS is W$_2$As$_3$. The composition of the WN$_x$ film can be measured either from the yield ratio of the N and W signals in the PRS spectrum or by comparing the height of the W signal from pure W film with that from the WN$_x$ film in the RBS spectrum.

The compositions of the WN$_x$ films for different N$_2$ partial pressure during sputtering, $\gamma$ as measured by RBS and PRS are summarized in Figure 3. The compositions measured by RBS agree well with that measured by PRS. The errors shown in Figure 3 are those in the PRS measurements. Note the linear dependence observed in this figure. This is in good agreement with the results of Uchitomi et al [11] who found that the nitrogen atomic percent in WN$_x$ film was nearly proportional to the N$_2$ content in the Ar-N$_2$ mixed gas.

After capless FA in As-overpressure in the temperature range of 700 to 850°C, RBS results for all WN$_x$/GaAs samples ($x=0$ to 0.5) show that a layer of W$_2$As$_3$ (~500Å) is formed on the top surface of the film. The nitrogen contents in these films, however, remain unchanged. This indicates that no detectable amount of N escape during annealing. In addition, no detectable interdiffusion at the W/GaAs and WN$_x$/GaAs interfaces is observed up to an annealing temperature of 850°C.
RBS measurements on capped WNₓ/GaAs samples formed with γ=20% FA in flowing N₂ in the temperature range of 700 to 850°C show similar compositional results as the capless FA samples except for the absence of the surface W₂As₃ layer in the capped samples. Capped samples (γ=20%) FA in As-overpressure at temperatures higher than 800°C result in the loss of nitrogen in the WNₓ films. After capped FA in As-overpressure at 850°C, x=0.18 while the as-deposited film has x=0.30.

No interfacial interaction can be detected in either W/GaAs or WNₓ/GaAs contacts after annealing. This is in apparent contradiction with our previous results on W/GaAs contacts in which we found interdiffusion at W/GaAs interface after capped FA in flowing N₂ at temperatures higher than 700°C [5]. This discrepancy will be discussed in the following sections.

2. Structural Analysis

The crystallographic structures of the films were studied using a x-ray Seeman-Bohlin diffractometer. Typical diffraction patterns of a WNₓ/GaAs sample before and after capless FA in As-overpressure are shown in Figure 4. For WNₓ films formed with γ<10%, XRD shows that the as-deposited films are the bcc α-W phase. As γ increases to ~10%, the as-deposited film becomes a defected β-W structure. Further increase in γ result in amorphous films. These results agree with the findings of So et al [15].

For WNₓ/GaAs samples treated with capless As-overpressure FA, XRD shows that all of the films transform into α-W and fcc W₂N with the amount of W₂N proportional to γ for γ=20 to 40%. An additional set of diffraction peaks corresponding to the monoclinic W₂As₃ phase is also observed in all annealed samples. This is in excellent agreement with the RBS results. A
summary of the XRD measurements for WN$_x$ films sputtered with different $\gamma$ before and after annealing is given in Figure 5.

The amount of W$_2$N phase in the WN$_x$ films are estimated from the integrated intensity of the W$_2$N (200) peak in the XRD spectra using the spectrum of the sample formed by sputtering at 1kW with $\gamma$=40% as a standard for W$_2$N film. This is shown in Figure 6 together with the values calculated from $x$ as measured by RBS and PRS. Note that these values agree reasonably well except for the case when $\gamma$=10%. The XRD spectrum of the WN$_x$ films formed with $\gamma$=10% ($x$=.1) only show $\alpha$-W phase. Therefore we must assume that some dispersed nitrogen atoms are present.

XRD spectra of WN$_x$ films FA with SiO$_2$ caps in As-overpressure at temperatures higher than 800°C show a drastic decrease in intensity of the W$_2$N diffraction peaks. No such decrease is observed for the capped samples FA in flowing N$_2$ or RTA in Ar. Amounts of W$_2$N phase as estimated from the (200) peak intensity for the capped samples ($\gamma$=20%) RTA at 950°C and FA in As-overpressure and flowing N$_2$ at 850°C are also shown in Figure 6 for comparison.

3. Film Resistivity and Stress

The resistivity of the WN$_x$ films as-deposited and after capless FA measured by four-point-probe as a function of $\gamma$ is shown in Figure 7. Note that the film resistivity increases with increasing nitrogen concentration in the film. The resistivity of a pure W$_2$N film ($\rho$=220 $\mu\Omega\text{-cm}$) is also included in the figure. This film was deposited with $\gamma$=40% and sputtering power of 1kW. The pure W$_2$N structure of this film is confirmed by XRD. From the RBS and XRD results, we know that the amount of W$_2$N phase in the
film is proportional to \( \gamma \) (Fig. 6). We therefore conclude that the increase in film resistivity as a function of \( \gamma \) is the direct result of increasing proportion of the \( W_2N \) phase in the film. We also observe in Figure 7 that for the same \( \gamma \), the resistivity is higher for as-deposited films. This is apparently the result of the defected or amorphous state of the film before annealing. Note also that the film formed with \( \gamma=10\% \) after annealing has \( \rho \) very close to that of pure \( W \) film. This is consistent with our XRD results which show that no \( W_2N \) phase is present in this film. For \( \gamma > 10\% \), \( \rho \) increases rapidly due to the formation of the high resistance \( W_2N \) phase in the film.

Figure 8 shows the stress of the films formed by sputtering with different \( \gamma \) for different total sputtering pressure. Only compressive stress is observed in all of the films studied in this work. Note that the film stress becomes less sensitive to the nitrogen content of the film as the total sputtering pressure increases. In fact for a total pressure of 20mT, the stresses of the films formed by sputtering with \( \gamma = 0, 10, 20 \) and 30\% are almost identical.

4. Diode Characteristics

The barrier height \( \Delta_b \) and ideality factor \( n \) of the \( WN_x/GaAs \) diodes formed with different \( \gamma \), as-deposited and capless FA in As-overpressure at 700, 800 and 850\(^{\circ}\)C are shown in Figure 9. The as-deposited diodes of \( W/GaAs \) and \( WN_x/GaAs \) with different N concentration show a common barrier height, \( \approx 0.59 \) eV. Since the ideality factors for these diodes are higher than 1.1 with excessive reverse leakage currents, they are "non-ideal". The fact that they show a common barrier is due to pinning by the native oxide at the
interface [16]. The barrier heights measured for these diodes therefore do not reflect the true barrier heights of the $\text{WN}_x$/GaAs interfaces.

After capless FA in As-overpressure at temperatures higher than 700°C, barrier heights of the W/GaAs and $\text{WN}_x$/GaAs diodes are significantly higher relative to the as-deposited diodes. In addition, the values of $n$ for all the annealed diodes decrease to below 1.08 indicating improvement of the diodes after annealing. Also, the barrier heights of the annealed W/GaAs diodes are smaller than those of the annealed $\text{WN}_x$/GaAs ($x>0$) diodes ($\Delta \Phi_B = 0.043$ eV). However, the values of $\delta_{bn}$ do not differ much ($\Delta \Phi_B = 0.01$ eV) for $\text{WN}_x$/GaAs diodes with different amount of nitrogen. The ideality factors of the diodes after annealing are consistently less than 1.08 indicating that the diodes are near "ideal" and thermionic emission is the dominant current transport mechanism in these diodes. No significant degradation is observed in these diodes even after capless FA in As-overpressure at 850°C.

Figure 10 shows the barrier heights and ideality factors of the $\text{WN}_x$/GaAs diodes formed with $\gamma=20\%$ as-deposited and annealed in different annealing conditions in the temperature ranges of 700 to 850°C for FA and 700 to 950°C for RTA. Diodes with ideality factors below 1.1 are obtained by capless FA in As-overpressure in the temperature range of 700-850°C and by capped RTA in the temperature range of 850-950°C. Diodes FA with caps in flowing $\text{N}_2$ show relatively less ideal diodes ($1.15>n>1.10$) probably due to voids or other interfacial defects in the contacts. An ideal diode is also achieved for capped FA in As-overpressure at 850°C after etching ~4000Å of GaAs from the peripheries of the diode. Figure 10 also shows that $\text{WN}_x$/GaAs diodes annealed with caps in different conditions achieve higher barrier heights than capless FA diodes. A barrier height close to 0.8 eV is obtained for capped FA diodes in As-overpressure at 850°C after mesa etching.
Diode characteristics ($\phi_b$ and $n$) of W/GaAs contacts as-deposited and annealed in different conditions at various temperatures are shown in Figure 11. Both the capped RTA and FA diodes in As-overpressure and flowing $N_2$ show non-ideal behavior ($n>1.20$) at temperatures higher than 700°C. W/GaAs diodes undergoing capless FA in As-overpressure, however, show improvement in $\phi_b$ and are found to be thermally stable up to 850°C.

IV. DISCUSSION

1. Effects of Nitrogen on The Thermal Stability and Barrier Heights of $WN_x$/GaAs Diodes

From the results displayed in Fig. 9 it is evident that the thermal stability of the $WN_x$/GaAs diodes is independent of the nitrogen concentration in the film. This is in agreement with the findings reported by Yamagishi [10] and Uchitomi et al. [11]. Geissberger et al. [12], however, found that diodes fabricated with 4 atomic percents of N exhibited the best thermal stability (up to 810°C) while diodes with 0, 11 and 21 atomic percents of N showed degradation after annealing at temperatures higher than 600°C. This low temperature degradation phenomenon for $WN_x$/GaAs diodes indicated that the nitride films were of very poor quality so that outdiffusion of dissociated Ga and/or As atoms proceed through grain boundaries and structural defects in the films.

The improved thermal stability of $WN_x$/GaAs contacts with $x>0$ is believed to be due to the presence of nitrogen atoms as impurities which stop the outdiffusion of Ga (and As) atoms. In other words, the $WN_x$ films in these contacts act as "stuffed" barriers to the underlying GaAs according to the
classification of thin film diffusion barriers by Nicolet [17,18]. In the case of pure W film on GaAs at high temperatures, the Ga (and As) atoms diffuse out rapidly along grain boundaries and other structural defects in the film. By adding nitrogen to the film, the nitrogen atoms tend to "plug" these diffusion paths and thus impede the diffusion. The fact that no W-N phase is detectable in the WN_x film formed with \( x = 10\% \) but yet good thermal stability is observed for contacts formed by this film is consistent with the "stuffed" barrier argument.

The maximum barrier heights we achieve for capless As-overpressure FA WN_x/GaAs diodes, with x ranging from 0.1 to 0.45, are independent of x and exhibit a common value =0.73±.1eV after annealing at 800°C for 30 min. This maximum barrier is significantly higher than that for pure W/GaAs diodes (=0.69eV). XRD results show that \( \alpha \)-W and W_2N are the two phases in the film after annealing. This strongly suggests that a very thin continuous layer of W_2N forms in intimate contact with GaAs so that the barriers measured in these contacts reflect that of W_2N/GaAs interface. This is supported by the I-V characteristics of a W_2N/GaAs diode after annealing at 800°C for 30 min which shows \( n=1.06 \) and \( \Delta E = 0.73\text{eV} \). In order to confirm the existence of this interfacial W_2N layer, cross-sectional transmission electron microscopy work is being carried out.

The improvement of the diode as seen in Fig. 9 upon annealing can be explained by the annealing out of defects due to sputtering damage at the interface forming good intimate contacts. This improvement has been observed for most metal/GaAs contacts formed under conventional diode fabrication procedures [16].
Our results also show a barrier enhancement of ≈0.04 eV for WNₓ/GaAs diodes comparing to the pure W/GaAs diode after annealing. The barrier enhancement for refractory metal nitride/GaAs contacts has been studied by Zhang et al [13] for ZrN, TiN and NbN on GaAs. They speculated that this enhancement of nitride contacts at high temperature was due to the nitrogen indiffusion creating a “camel-diode” structure [19] where a p-like layer was created near the metal/GaAs interface. However, the exact role played by N atoms in GaAs is not well known.

This enhancement phenomenon is also consistent with the amphoteric defect model suggested recently by Walukiewicz [20]. According to this model, the barrier heights for metal/GaAs contacts are limited by the charge states of gallium vacancy V₉Ga (1-/2-) and V Ga (2-/3-). The barrier height of a particular metal/GaAs contact is also determined by the metal electronegativity x. Since W is a electropositive metal, x =1.7 (Pauling scale), a low barrier is expected for W/GaAs contact. While N is a very electronegative element, the effective electronegativity for the W₂N phase in intimate contact with GaAs is higher than that of W. Therefore a higher barrier is expected for the WNₓ/GaAs contacts.

2. Effects of Annealing Conditions on The Thermal Stability and Barrier Height of WNₓ/GaAs Contacts

W/GaAs contacts are found to be structurally and electrically stable even after capless FA at 850°C for 30 min in As-overpressure as shown in this work. Diode degradations (n>1.1 with high leakage currents) are observed for W/GaAs diodes capped FA in both As-overpressure and flowing N₂ at temperatures higher than 700°C. These results are consistent with our
previous work on cap-annealed W/GaAs diodes [5] where these degradations were explained by the inter-diffusions at the W/GaAs interface.

Recently, Pugh and Williams [21] calculated the chemical interactions between gold and nine III-V compound semiconductors using bulk thermodynamic properties. They showed that the entropy of formation of the gas-phase group V element is the major driving force in metal/III-V reactions. Their results also indicated that in the presence of gas-phase group V overpressure at high temperature, the dissociation of III-V at the interface is minimized and therefore entropy-driven interfacial reactions can be suppressed. It is also known that for the high temperature annealing (>700°C) of SiO₂ capped GaAs, Ga atoms tended to diffuse out to the cap layer [22, 23]. This supports our previous results of SiO₂ cap-annealed W/GaAs contacts. In these diodes only islands of W₂As₃ phase were observed after annealing at temperatures higher than 750°C. The absence of a W-Ga phase can be explained with the out-diffusion of the Ga atoms to the cap. In the present study, W₂As₃ islands are not found to form at the W/GaAs interface in the cap-annealed contacts. This is probably because of the better quality W films obtained in this work (our as-deposited films assume the α-W phase while in Reference 5, the as-deposited W film is the defected β-W phase). However, interfacial interdiffusions may still occur in our cap-annealed W/GaAs contacts. The sensitivity of the RBS technique (>10¹⁷ atoms/cm³) is not sufficient to reveal the W atoms which may have diffused into the GaAs substrate. On the other hand electrical effects which could explain the electrical degradation of the junctions become important at W concentrations much smaller than the RBS limit.
For \( WN_x/GaAs \) contacts, cap-annealing results in close to ideal diodes up to an annealing temperature of 850°C for FA and 950°C for RTA. \( WN_x/GaAs \) diodes capped FA in As-overpressure at temperatures higher than 800°C show drastic degradation in the diode characteristics. Ideal diode behavior is resumed after etching off ~4000Å of GaAs from the peripheries of these diodes. Scanning electron microscropy (not shown) investigations show that voids appear along the edge of this diode before etching. Such structural defects represent centers of high electric field when the diode is under bias causing the high leakage current and the non-ideal rectifying behavior of the diode. This effect is however not observed for diodes annealed in flowing \( N_2 \) ambient. This can also be understood with the concept of stuffed barrier. The SiO\(_2\) layer on GaAs simply acts as a diffusion barrier. In the presence of a \( N_2 \) ambient, the diffusion paths in the SiO\(_2\) film are "stuffed" by the nitrogen atoms incorporated in the film. The SiO\(_2\) layer therefore becomes a very efficient cap for the dissociated GaAs at the interface.

Note also that the capped As-overpressure FA \( WN_x/GaAs \) diodes achieve a much higher barrier height (\( \Phi_0 = 0.8 \) eV) than the diodes annealed under other conditions. This result is again consistent with the observation that a significant amount of nitrogen is lost in these \( WN_x \) films which renders the films less efficient as diffusion barriers to the Ga (and As) atoms. Hence an As-rich layer develops below the metal layer during high temperature annealing. Since a large concentration of Ga vacancies, which are acceptors in GaAs, exist in the As-rich layer, the layer becomes p-type. Therefore a camel-diode structure [19] may result giving rise to an increased barrier height. Nevertheless, if the N atoms in the \( WN_x \) film in-diffuse to the GaAs
substrate rather than out-diffuse to the SiO₂ encapsulant, it may also be possible that the barrier enhancement is due to the N incorporation in GaAs as has been suggested by Zhang et al [13].

Capped RTA WNₓ/GaAs diodes show very good thermal stability up to 950°C. This is because the short annealing duration is too rapid for any significant diffusion yet allows sufficient time for film crystallization and intimate contact formation.

V. CONCLUSIONS

The most important results from these studies are:

1. The amount of nitrogen incorporated in the WNₓ film is directly proportional to the N₂ partial pressure during sputtering.
2. For γ<40%, α-W and W₂N are the only two phases present in the WNₓ film after annealing at temperatures higher than 700°C.
3. Schottky barrier heights for WNₓ/GaAs (with x≠0) contacts are found to be insensitive to the amount of nitrogen in the film. It is believed that this is the result of a thin continuous layer of W₂N phase in intimate contact with GaAs.
4. Thermal stability of WNₓ/GaAs interfaces are found to be insensitive to the annealing environment. This is believed to be the results of the good diffusion barrier formed by the film in which the diffusion paths are "stuffed" by the nitrogen atoms.
5. Thermal stability of elemental W/GaAs interface is greatly influenced by the annealing conditions. SiO₂ capping layers are found to induce interfacial instability in these contacts at high temperatures.
6. For As-overpressure annealing, comparing with the W/GaAs contacts, the increase of barrier heights of WN_x/GaAs contacts is thought to be caused by the increased effective electronegativity of the W2N phase which is in intimate contact with GaAs.

7. WN_x/GaAs diodes annealed with SiO_2 cap in As-overpressure show further barrier enhancement. This is believed to be the effect of the SiO_2 induced Ga-outdiffusion resulting in an As-rich interfacial layer below the metal.
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REFERENCES


FIGURE CAPTIONS

Fig. 1 2.0 MeV $^4$He$^+$ RBS spectra of WN$_x$/GaAs ($\gamma$=40\% ) samples as-deposited (square spectrum) and capless FA in As-overpressure at 850°C (solid line spectrum). Note the formation of a surface layer of W-As phase in the annealed sample.

Fig. 2 1.675 MeV PRS spectra of the as-deposited sample as in Fig. 1. The enhanced nitrogen backscattering signal in the spectra facilitates the accurate compositional analysis of these samples.

Fig. 3 A plot of the nitrogen concentration of the WN$_x$ films formed by different sputtering N$_2$ partial pressure $\gamma$ as measured by RBS and PRS.

Fig. 4 (a) and (b) Glancing angle XRD spectra of the same set of samples as in Fig. 1.

Fig. 5 A summary of the XRD measurements of the WN$_x$ films as-deposited and capless FA in As-overpressure at temperatures higher than 700°C for films with different nitrogen contents $x$.

Fig. 6 Plots of the amounts of W$_2$N phase in the WN$_x$ films after capless FA in As-overpressure at 700°C as a function of $\gamma$ as calculated from $x$ (solid line) and from the intensity of the W$_2$N (200) diffraction peak in the XRD spectra (dashed line). Values for samples ($\gamma$=20\%) capped RTA at 950°C and FA in As-overpressure and flowing N$_2$ are also included for comparison.

Fig. 7 Film resistivity $\rho$ of WN$_x$ films as deposited and capless FA in As-overpressure as a function of $\gamma$. Resistivity values for pure $\alpha$-W and W$_2$N films are also shown.

Fig. 8 Plots of film stress as a function of the total sputtering pressure for different $\gamma$. 
Fig. 9 Plots of barrier heights, $\phi_B$ and ideality factors, $n$ as a function of the annealing temperature (capless FA in As–overpressure) for \( WN_x/GaAs \) diodes formed by different $\gamma$.

Fig. 10 Plots of $\phi_B$ and $n$ as a function of annealing temperature under different annealing conditions for \( WN_x/GaAs \) diodes formed by $\gamma=20\%$.

Fig. 11 Plots of $\phi_B$ and $n$ as a function of annealing temperature under different annealing conditions for elemental W/GaAs diodes.
2.0 MeV He-RBS
WN\textsubscript{X}/GaAs: \gamma = 40\%
SQUARE: As-deposited
SOLID: FA: 850°C
in As-overpressure

ENERGY (MeV)

COUNTS/CHANNEL

CHANNEL #
Fig. 3
Fig. 4
Fig. 5
- Calculated from x
- Measured from XRD
- Capped FA in As-overpressure (850°C)
- Capped FA in Nitrogen (850°C)
- Capped RTA (950°C)

Fig. 6
Resistivity $\rho$ ($\mu\Omega \cdot \text{cm}$)

- as-deposited
- 850 °C 30 min.

$\gamma$ (%)
WNx/GaAs: COMPRESSION STRESS

3000 Å WNx FILM

\[
\frac{P(N2)}{P(N2 + Ar)}
\]

- X 0.0%
- O 10.0%
- ● 20.0%
- △ 30.0%
- ▲ 40.0%

STRESS [10^9 DYNE/CM^2]

TOTAL PRESSURE, P(N2 + Ar) [mT]

Fig. 8
Fig. 9
Fig. 10
Figure 11