Харьковская нанотехнологическая Ассамблея

ТОНКИЕ ПЛЕНКИ В ОПТИКЕ И НАНОЭЛЕКТРОНИКЕ

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Разделы

- Методы синтеза тонких пленок и обработки поверхностей в оптике и наноэлектронике
- Инженерные технологии наноразмерного диапазона
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Том 2

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Сборник докладов
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Под общей редакцией И.М. Неклюдова, В.М. Шулаева

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Сборник докладов 18-го Международного симпозиума «Тонкие пленки в оптике и наноэлектронике». – Харьков: ННЦ «ХФТИ», ИПП «Контраст», 2006. — с. 428.

Представлены материалы 18-го Международного симпозиума «Тонкие пленки в оптике и наноэлектронике» состоявшегося в г. Харьков 2-6 октября 2006 г. В публикуемых докладах обсуждаются достижения в области разработок новых методов синтеза тонких пленок и обработки поверхностей, инженерные технологии наноразмерного диапазона, а также свойства наноалмазных пеленок и наноструктурных пленок родственных материалов. Рассматриваються вопросы нанометрологии и наноаналитики.

Сборник трудов Ассамблеи может быть полезен научным и инженерно-техническим работникам, специализирующимся в области вакуумных нанотехнологий и оборудования.

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TECHNOLOGY AND COMPARATIVE INVESTIGATION OF TERNARY W-TiN AND Ta(Ti)-SiN THIN FILM DIFFUSION BARRIERS

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A comparative investigation of W-Ti-N, Ta-Si-N and Ti-Si-N thin films, deposited by reactive magnetron sputtering of W-Ti (30 at.%), Ta_5Si_3 and Ti_5Si_3 targets, respectively, in a various gaseous mixture of Ar/N_2 is presented. The chemical and phase compositions, electrical conductivity, thermal stability as well as diffusion barrier performances of investigated W-TiN and Ta(Ti)-SiN thin film diffusion barriers, have been study using Rutherford backscattering spectrometry (RBS), X-ray diffraction (XRD), four-point probe sheet resistance measurements, secondary ion mass spectrometry (SIMS), optical and atomic force microscopy (AFM).

1. INTRODUCTION

Gold based metallization is still good and wide employed in technology of GaAs devices and related ICs. A one disadvantage of this metallization is reactivity of gold with GaAs in working devices at enhanced temperature. This leads to reducing stability of parameters and lifetime of devices. Many works in last 20 years were devoted to elimination or suppression the Au-GaAs reaction by introducing a diffusion barrier separating contact region from gold overlayer used as interconnection lines and wire paths.

Good diffusion barriers promote the low diffusivity of metals, low resistivity and the high thermal and chemical stability of the thin film in semiconductor high-temperature metallization. The exceptional combination of properties of transition metal (TM)-nitride as well as TM-Si-N films such as fairly low resistivity, amorphous, thus free of fast diffusion paths microstructure, high thermal and chemical resistance makes these materials of choice for diffusion barriers in metallization systems to semiconductor devices.

This work will show an approach of W-Ti-N, Ta-Si-N and Ti-Si-N thin film diffusion barriers technology for gold-based metallization to GaAs devices.

2. EXPERIMENTAL PRPOCEDURE

Thin films of W-Ti-N, Ta-Si-N and Ti-Si-N were prepared by magnetron sputtering from W-Ti (30 at.%), Ta_5Si_3 and Ti_5Si_3 targets, respectively, in Ar (purity: 99.999 %) and Ar/N_2 (purity: 99.999 %) gas mixture, using Leybold Universal Coating System (Fig. 1). Parameters of deposition: **W-Ti-N** (target power 300 W; nitrogen partial pressure P_{N2} = 0-0.35 Pa; total gas pressure $P_{Ar}+P_{N2}$ ~0.5 Pa); **Ta-Si-N** (target power 200 W; nitrogen flow f_{N2} =0-20 sccm; argon flow f_{Ar} = 100-130 sccm; total gas pressure $P_{Ar}+P_{N2}$ ~ 0.5 Pa); **Ti-Si-N** (target power 450 W; nitrogen flow f_{N2}=0-15sccm; argon flow f_{Ar}=150sccm; total gas pressure $P_{Ar} + P_{N2}$ ~ 6.5 Pa).

The GaAs (100) substrates were cut into 10×10 mm pieces, degreased in organic solvents in an ultrasonic bath (trichloroethylene, acetone, methanol), and following etched.

Films, as-deposited and annealed structure Au/films/GaAs, were characterized by RBS, XRD, SIMS, AFM, four-point probe sheet resistance measurements and optical microscopy.

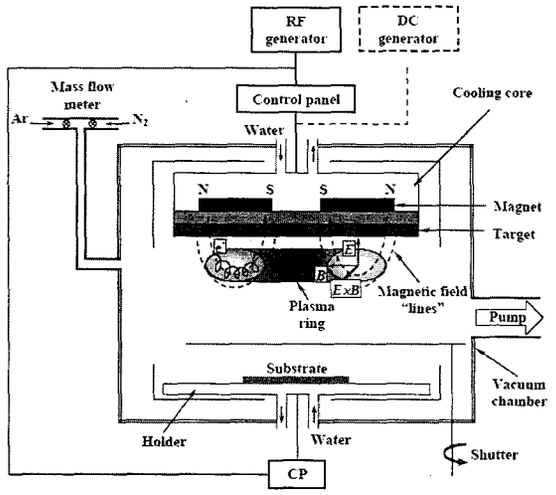

Fig.1. Design of magnetron sputtering system for deposition of thin films

3. RESULTS AND DISCUSSION

3.1. W-Ti-N THIN FILMS

The influence of nitrogen partial pressure (P_{N2}) on the W-Ti-N film chemical and phase composition, electrically resistivity is shown in Fig. 2. 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 [1]. 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).

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 $W_{64}Ti_{16}N_{20}$ film deposited at P_{N2}=0.02 Pa, indicating in complex character of the phase changes which occur when the nitrogen content of the films increases. Ternary $W_{64}Ti_{16}N_{20}$ 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 ($W_{1-y-x}Ti_xN_y$).

From the dependences of reactively sputtered W-Ti-N films resistivity on partial pressure of nitrogen P_{N2}, it can be seen that electrical resistivity of as-deposited W-Ti-N thin films increases with increasing of P_{N2}. The increasing takes place due to a gradual incorporation of nitrogen atoms into the films. The resistivity of pure binary $W_{78}Ti_{22}$ film (formed only with argon gas) is about 118 μΩ·cm and rises slowly up to 370 μΩ·cm for the ternary $W_{43}Ti_{12}N_{45}$ film. The film resistivity increases steeply, if the nitrogen concentration exceeds 45 at.%. The increasing of film resistivity can be caused by following reasons: (i) electron scattering by incorporated Ti and N atoms in the W lattice which acts as impurities; (ii) the saturation of the matrix with nitrogen atoms (decreasing of metal atoms amount and increasing of correspondent inter-atomic distances); (iii) formation of nitride phases. The abrupt increasing of resistivity for films containing nearly the same number of nitrogen atoms (from 50 to 55 at.%) can be attributed to the grain size decreasing. It is about 20 nm for $W_{40}Ti_{10}N_{50}$ (497 μΩ·cm) and about 14 nm in the case of $W_{34}Ti_{11}N_{55}$ (894 μΩ·cm).

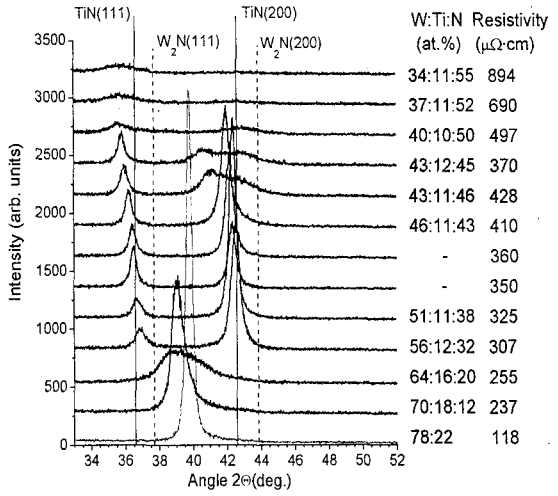

Fig. 2. XRD diagrams, composition and resistivity of as-deposited W-Ti-N thin films

For GaAs/$W_{64}Ti_{16}N_{20}$/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 [1]. The RBS spectra of as-deposited and annealed at 750°C samples overlap (Fig. 3), indicating that intermediate a $W_{64}Ti_{16}N_{20}$ barrier prevents the interaction between Au and GaAs. It is obvious that this barrier fails as a result of annealing at 800°C.

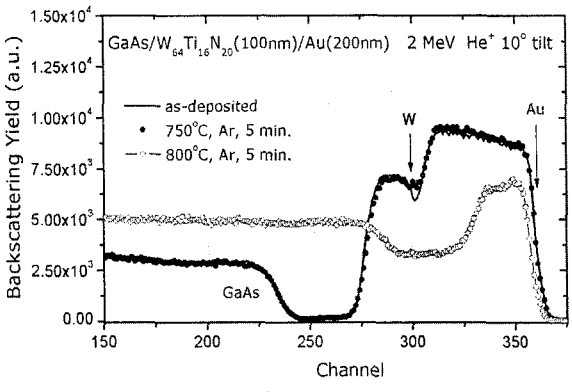

Fig. 3. RBS spectra from as-deposited and annealed at 750 and 800°C (Ar, 5 min.) GaAs/$W_{64}Ti_{16}N_{20}$/Au structures

3.2. Ta-Si-N THIN FILMS

Ta-Si-N films are X-ray amorphous in the as-deposited state, exhibited broad diffraction "halo" characteristic of an amorphous material (Fig. 4). With increasing nitrogen content, the position of the diffraction peak shifts to low angles and peak with at half maximum increase, indicating a change of the shot-range order of the Ta and Si atoms (the average

distance between atoms increase). Increase of the "degree of amorphism" agrees with change of chemical composition and an increase of Ta-Si-N films resistivity. It has been shown [2,3], that the increase in amount of nitrogen in sputtering plasma leads to: (i) increase of nitrogen concentration and decrease of Ta/Si atomic ratio in the films, due to the incorporation into the film of nitrogen atoms from the plasma; (ii) increase of crystallization temperature of the films; (iii) increase of films electrical resistivity.

Sharp increase of resistivity and amorphous nature of the high N containing films is due to the fact that fraction of silicon nitride $Si_{1-x}N_x$ (nonconducting and amorphous) rises and of tantalum nitride $Ta_{1-x}N_x$ (conducting and polycrystalline) decreases, with increase of nitrogen content in sputtering plasma [4]. These films may be viewed as a mixture of tantalum nitride imbedded in a silicon nitride amorphous matrix, what has been described in [5]. This model explain microstructure, thermal stability and excellent diffusion barrier performance of ternary Ta-Si-N thin films with N content more than 40 at.%. As was be shown in [2], the XRD investigation of $Ta_{34}Si_{25}N_{41}$ film, show no changes in amorphous state, up to annealing at 900°C in Ar flow for 5 min. $Ta_{34}Si_{25}N_{41}$ film crystallised at 1000°C and formed Ta_5Si_3 and $TaN_{0.8}$ phases.

For diffusion barrier applications, the resistivity values of as-deposited thin films must be below of 1000 μΩ cm [5].

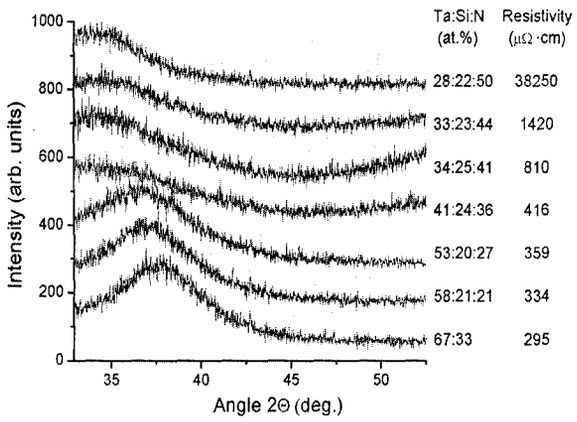

Fig. 4. XRD diagrams, composition and resistivity of as-deposited Ta-Si-N thin films

At that point the Ta-Si-N films, contains below 34 at.% of tantalum, 25 at.% of silicon, 41 at.% of nitrogen atoms, having resistivity less by 810 μΩ cm was chosen for diffusion barrier performance investigations, in Au-GaAs contact metallization.

A result of investigations of antidiffusion properties of Ta-Si-N thin films [2-4], shows that $Ta_{34}Si_{25}N_{41}$ exhibits excellent diffusion barrier properties. The sheet resistance of $Au/Ta_{34}Si_{25}N_{41}/GaAs$ structure remains nearly unchanged up to annealing temperature of 800°C, indicating in no-interaction between contact metallization systems and substrate. That assumption is confirmed by RBS analysis of structure depth profiles distribution of elements. The RBS spectra for as-deposited and annealed at 800 °C samples overlap (Fig. 5), indicating that the intermediate amorphous $Ta_{34}Si_{25}N_{41}$ film totally prevented the interaction between Au and GaAs.

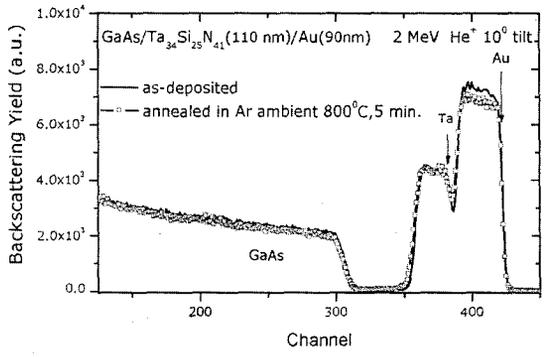

Fig. 5. RBS spectra of $GaAs/Ta_{34}Si_{25}N_{41}/Au$ samples, before and after annealing in Ar at 800°C for 5 min

3.3. Ti-Si-N THIN FILMS

The compositions of Ti-Si-N thin films sputter-deposited in various N_2/Ar flow ratios are shown in Fig. 6. The N concentration increase and the content of Ti and Si atoms decrease with increasing nitrogen-to-argon flow ratio, with a tendency to saturation for

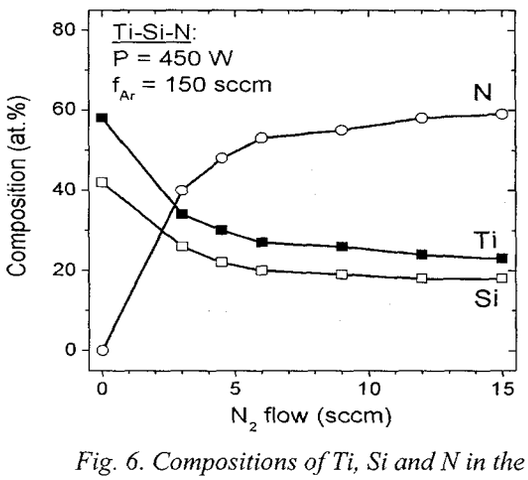

Fig. 6. Compositions of Ti, Si and N in the reactively sputtered Ti-Si-N films, as a function of N_2 flow

large flow ratio. The N content in the films increases from 0 to 59 at.% as N_2/Ar ratio increases from 0 to 15 %, because a greater number of reactive nitrogen

incorporate into the film during the sputtering process.

The Ti/Si ratio in nitrogen-free Ti-Si film is 1.4, as well compared to 1.6 in Ti_5Si_3 target material, which indicates preferential sputtering with Ti enrichment. By adding nitrogen to the sputtering plasma, this ratio remain nearly unchanged indicating in similar sputtering yields of the Ti and Si component, with changing of sputtering conditions.

For higher nitrogen amounts, the decrease of Ti content in Ti-Si-N films was noted.

Fig. 7 shows the resistivity of as-deposited Ti-Si-N thin films as a function of N_2 flow. When the N_2/Ar flow ratio is lower than 4 %, the electrical resistivity rose slowly from approximately 312 μΩ cm for $Ti_{58}Si_{42}$ film up to 1000 μΩ cm for the ternary $Ta_{27}Si_{20}N_{35}$ film. But, when the flow ratio is higher than 4 %, nitrogen content in the Ti-Si-N films exceeds 53 at.% and the resistivity increases abruptly to ~ 3000 μΩ cm and larger. A $Ta_{23}Si_{18}N_{59}$ (at N_2/Ar = 10 %) film has about 26600 μΩ cm. Increase of resistivity may be attributed to increase content of nonconducting $Si_{1-x}N_x$ fraction, and decrease of conducting $Ta_{1-x}N_x$ fraction.

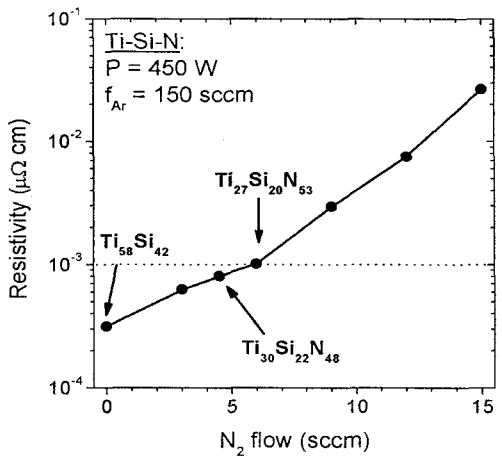

Fig. 7. Resistivity of reactively sputtered Ti-Si-N films, as a function of N_2 flow

Fig. 8 shows the sheet resistance changes for various GaAs/Ti-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 resistivity of both semi-insulating GaAs substrate and Ti-Si-N barrier layer exceeded that of Au film). For Ti-Si-N barrier layers, first annealing steps at 400°C caused the decrease of sheet resistance by about 20% for all 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.

An increase of sheet resistance for GaAs/$Ti_{34}Si_{26}N_{40}$/Au and GaAs/$Ti_{30}Si_{22}N_{48}$/Au samples, after annealing at > 600°C indicates that these barriers failed. For GaAs/$Ti_{26}Si_{18}N_{57}$/Au sample, barrier degradation begins after annealing at 700°C.

In contrast, for GaAs/$Ti_{27}Si_{20}N_{53}$/Au and GaAs/$Ti_{26}Si_{19}N_{55}$/Au samples, the sheet resistance remains nearly unchanged up to annealing temperature of 800°C. Ti-Si-N films with nitrogen concentration from 53 to 55 at.% prevent interactions between Au and GaAs temperatures up to 800°C.

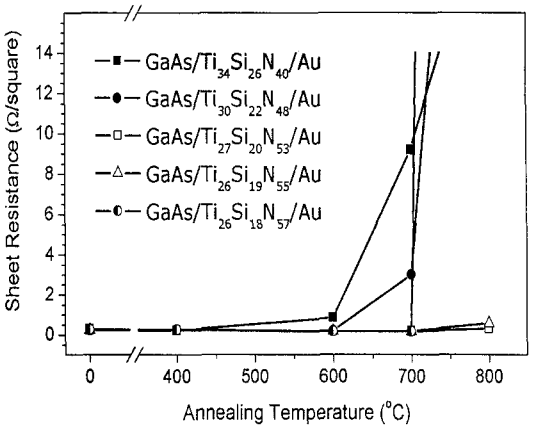

Fig. 8. Sheet resistance of GaAs/Ti-Si-N/Au samples annealed at temperatures from the range 400 to 800°C

4. CONCLUSIONS

The relationship between magnetron deposition parameters (especially, nitrogen content in sputtering plasma) and properties (chemical and phase compositions, electrical resistivity, thermal stability, diffusion barrier performance) of W-TiN and Ta(Ti)-SiN thin films has been studied.

The model, explanation the correlation between deposition parameters, formation mechanism and properties of W-TiN and Ta(Ti)-SiN thin films has been proposed.

By optimizing the parameters of sputter deposition, the 100 nm thick thin film diffusion barriers, prevents the interaction between Au and GaAs under annealing at 750°C for $W_{65}Ti_{17}N_{18}$, and at 800°C for $Ta_{34}Si_{25}N_{41}$, $Ti_{27}Si_{20}N_{53}$ and $Ti_{26}Si_{19}N_{55}$. This fact indication on usefulness of W-TiN and Ta(Ti)-SiN thin films, in high temperature and high power electronics application.

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ТЕХНОЛОГИЯ И СРАВНИТЕЛЬНОЕ ИССЛЕДОВАНИЕ ТРОЙНЫХ ТОНКОПЛЕНОЧНЫХ ДИФФУЗИОННЫХ БАРЬЕРОВ W-TiN И Ta(Ti)-SiN

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Представлено сравнительное исследование тонких пленок W-Ti-N, Ta-Si-N и Ti-Si-N, полученных реактивным магнетронным распылением мишеней W-Ti (30 ат.%), Ta_5Si_3 и Ti_5Si_3 соответственно, при различных соотношениях Ar/N_2 в газовой смеси. Химический и фазовый состав, электрическое удельное сопротивление, термическая стабильность и антидиффузионные свойства исследуемых тонкопленочных диффузионных барьеров W-TiN и Ta(Ti)-SiN проводились с использованием метода резерфордовского обратного рассеяния (РОР), рентгеновской дифракции (РД), четырехзондового метода, вторично-ионной масс спектрометрии (ВИМС), оптического и атомно-силового микроскопа