JOURNAL OF MATERIALS SCIENCE 21 (1986) 1675–1680

Interaction of TiW film with GaAs

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The interactions of co-evaporated $Ti_{0.3}W_{0.7}$ films with GaAs have been studied after annealing at temperatures in the range of 650 to 900° C for 15 min employing Rutherford backscattering, transmission and scanning electron microscopy, X-ray diffraction and energy-dispersive X-ray analysis techniques. Reaction has been found to take place at 650° C as evidenced by the presence of an AsTi compound in the region near the interface of TiW film and GaAs. Gallium diffuses out to the surface at temperatures above 750° C and causes surface morphological degradation, which can be related to the instability of the TiW Schottky barrier height at higher temperatures $\gtrsim$ 750° C as reported in the literature.

1. Introduction

A considerable amount of work has recently been done to develop GaAs high-speed digital integrated circuits based on various logic circuits which are normally comprised of GaAs MESFETs [1, 2]. The main problem with this type of device fabrication technology is the high parasitic resistance of GaAs MESFETs [3]. Yokoyama *et al.* [3] have proposed self-aligned implantation technology to significantly reduce the parasitic source series resistance, so as to realize high-speed switching performance. High-temperature annealing is needed to activate the implanted dopants and therefore the material used for making Schottky gates must be metallurgically stable at high temperature. The TiW system has been widely used in metallizing silicon to integrated circuits because it has good adhesion to silicon and acts as a diffusion barrier [4]. TiW metallization has also been studied for the formation of Schottky barriers in GaAs analogue and digital integrated circuits using both diodes and MESFETs [5].

Kohn [6] reported that TiW films on GaAs remain unalloyed up to 860° C and that they exhibit constant diode characteristics at temperatures of up to 800° C. Yokoyama *et al.* [3] have studied the Schottky barrier height and ideality factor of TiW gate contacts on GaAs as functions of annealing temperature, and found a considerable increase in ideality factor and reduced barrier height; there is also a greater irregularity in these parameters. Employing Rutherford backscattering and secondary-ion mass spectroscopic techniques, Yokoyama *et al.* [3] have shown that reaction takes place between TiW films and GaAs at temperatures as low as 750° C, and that this metallurgical reaction results in instability of the TiW Schottky barrier electrical characteristics.

No detailed work has so far been reported on the phase formation and surface morphology of TiW films on GaAs as a function of annealing temperature. In this paper we report the results of a detailed investigation of the reaction and compound formation of TiW on GaAs Schottky gate contacts using scanning electron microscopy (SEM), transmission electron microscopy and diffraction (TEM, TED), X-ray diffraction, energy-dispersive analysis of X-rays (EDAX) and Rutherford backscattering (RBS) techniques.

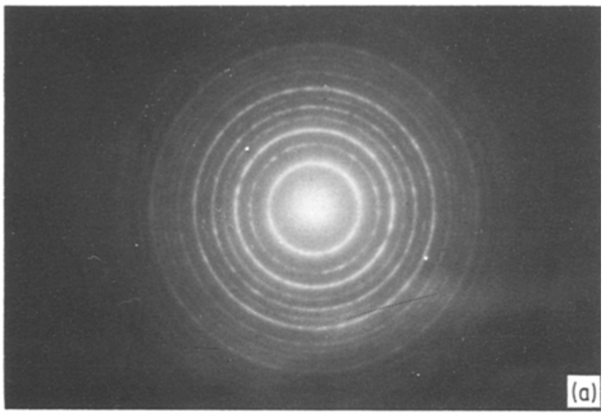
2. Experimental procedure

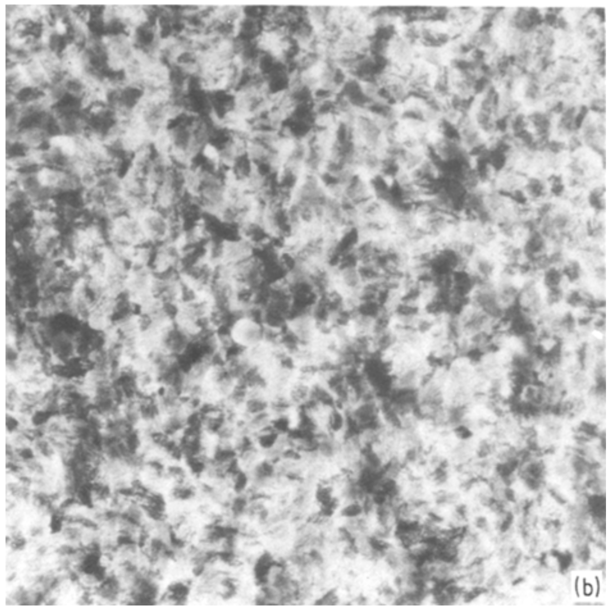
Undoped GaAs (1 0 0) substrates were used in the present study. Prior to the deposition of metal films, the substrates were dipped into 2% HF solution for 0.5 min and then rinsed with trichloroethylene, acetone and methanol. The TiW film was sputter-deposited from a hot-pressed TiW composite in the ratio 10 : 90 by weight (30 : 70 atomic). This mixture has commonly been used in interconnect metallization as it provides good corrosion resistance compared with other refractory metals [7]. The background pressure in the deposition chamber was 10^{-6} torr. The films were capped with low-temperature plasma-deposited Si_3N_4 of thickness ~ 100 nm. The annealing was done in a furnace under N_2 atmosphere at 650, 750, 850 and 900° C for 15 min.

Plan-view TEM specimens (2 mm × 2 mm) were made by chemical jet thinning from the back side using a bromine–methanol solution. To obtain direct information about the interface we made cross-sectional TEM specimens in some cases. The specimens were made by mechanical polishing up to 50 to 60 μm and then ion-milling using 5 keV Ar^+. TEM and SEM studies were done on a Hitachi H–600 scanning transmission electron microscope operated at 100 and 25 keV, respectively. However, a few measurements were also made using a JSM–35CF scanning microscope (25 keV) with EDAX attachment. Rutherford backscattering measurements were performed using a 3 MeV $^4He^+$ ion beam from a tandetron accelerator. The thickness of the TiW film was measured by backscattering and found to be ~ 100 nm.

3. Results and discussion

Fig. 1a represents the transmission electron diffraction pattern of the as-deposited TiW film on GaAs substrate. The presence of diffraction rings clearly indicate the polycrystalline nature of the film. Careful





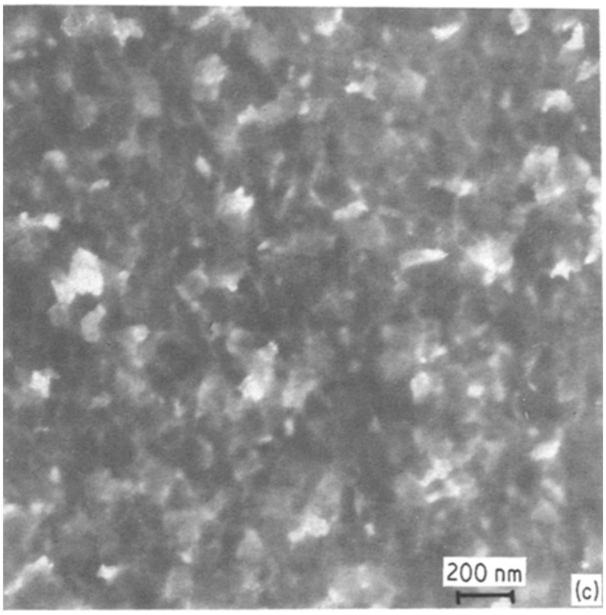


Figure 1 (a) TED pattern (b) bright-field and (c) dark-field micrographs of the as-deposited TiW film on GaAs.

analysis of the diffraction pattern shows that only the diffraction rings corresponding to tungsten are present. No evidence of titanium diffraction rings have been found. The absence of titanium diffraction rings is possibly due to the low volume fraction of titanium in TiW film. Figs. 1b and c represent the strong-beam bright-field and the corresponding dark-field micrographs of the as-deposited TiW film. Tungsten grain sizes varying from 40 to 160 nm are clearly visible in Fig. 1c. A plan-view TEM specimen of TiW/GaAs annealed at 650° C for 15 min was examined in the electron microscope. The TED pattern of the near-surface region (that is the region close to the TiW surface) of the annealed specimen appeared exactly similar to that of the as-deposited film, indicating that no reaction between titanium and tungsten has taken place after annealing at 650° C.

In order to see whether any reaction had occured near the interface of TiW film and GaAs at 650° C, part of the film was sputtered from the surface of the same TEM specimen by iɔn-milling. The thin area then consisted of both the GaAs substrate as well as the TiW film. Figs. 2a and b show the bright-field micrograph and TED pattern, respectively, of the interface region of TiW layer and GaAs substrate. The TED pattern consists of both polycrystalline diffraction rings as well as single-crystalline diffraction spots,

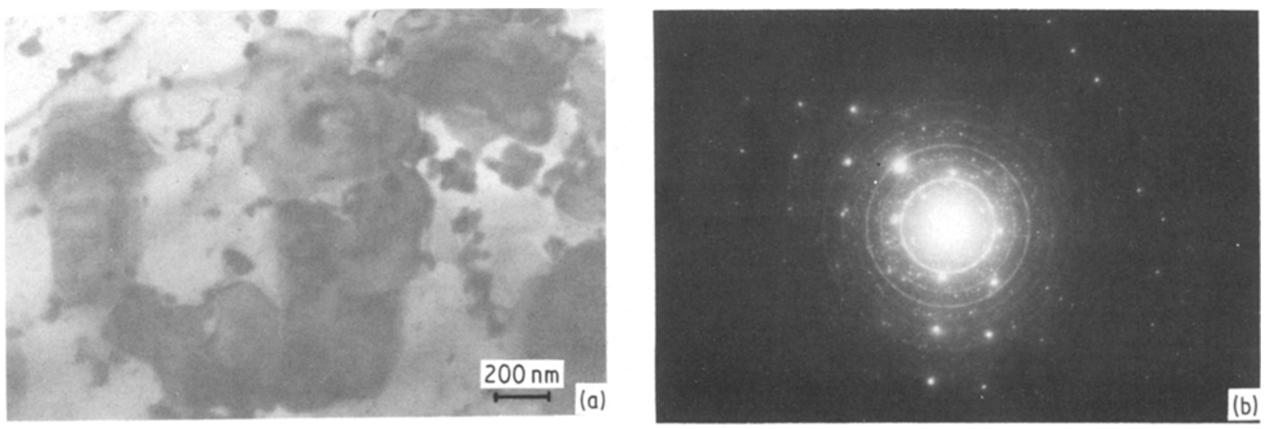
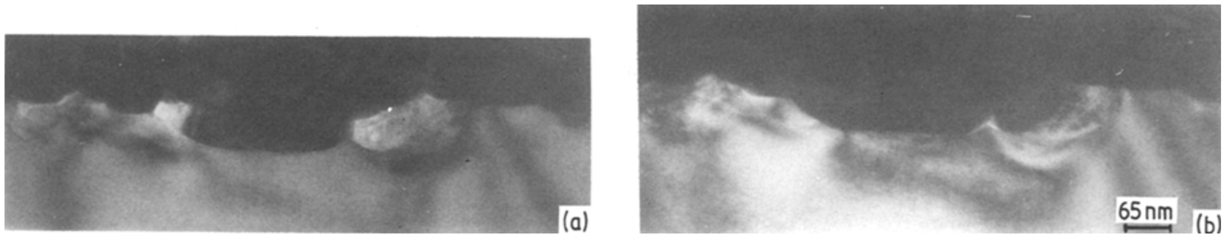


Figure 2 (a) Bright-field mirograph and (b) TED pattern of the interface region of TiW layer and GaAs substrate of 650° C annealed specimen.



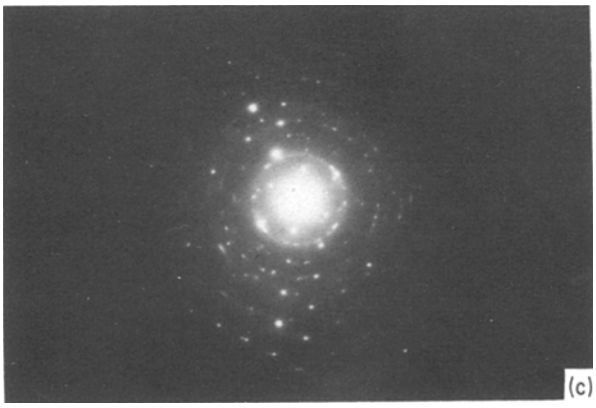


Figure 3 Cross-sectional (a) bright-field (b) dark-field micrographs and (c) corresponding TED pattern of 850° C annealed specimen. In (a) and (b) the surface is at the top of each picture.

the latter due to the underlying GaAs substrate. The polycrystalline diffraction rings were carefully analysed and their *d* values evaluated employing standard techniques. It was found that some of the observed *d* values matched well with those of pure tungsten, while others matched well with those of the hexagonal AsTi compound (See Table I). This clearly indicates that at the interface region the titanium of the TiW film reacted with GaAs at 650° C, while tungsten did not react with GaAs.

The formation of an AsTi compound at the interface was also verified from the X-ray diffraction studies. The X-ray diffraction pattern of the TiW/GaAs system annealed at 650° C for 15 min was found to contain, in addition to the peaks due to titanium and tungsten, two extra peaks at 2θ values of 32 and 36.2°, corresponding to 1 0 2 and 1 0 3 reflections of the hexagonal AsTi compound. TED and X-ray diffraction patterns of the TiW/GaAs system annealed at 750° C show essentially similar features to the 650° C annealed specimen.

Figs. 3a, b and c represent the cross-sectional strong-beam bright-field micrograph, the conventional dark-field micrograph and the corresponding selected-area diffraction pattern, respectively, of the 850° C annealed specimen. In the TED pattern, single-crystal diffraction spots as well as polycrystalline diffraction rings are found to be present. Standard analysis of the diffraction pattern shows that the single-crystal diffraction spots are due to the GaAs substrate. While most of the polycrystalline diffraction rings are due to tungsten, some diffraction rings due to AsTi are also observed. As is evident from the bright-field micrograph, the interface of the TiW film and GaAs substrate is rough, indicating that the reaction at the interface has not taken place uniformly.

The X-ray diffraction pattern of the 900° C annealed specimen was taken and found to be similar to that of the 650° C anneal specimen. No indication of the reaction of tungsten with titanium and/or with GaAs was observed. To study the diffusion processes in the TiW/GaAs system annealed at various temperatures, we performed Rutherford backscattering analysis and the results are described below. Fig. 4 shows the RBS spectra of as-deposited and two annealed (750 and 850° C, both for 15 min) TiW films deposited on GaAs. From the spectrum of the as-deposited film, the composition of titanium and tungsten and the film thickness can be calculated. The

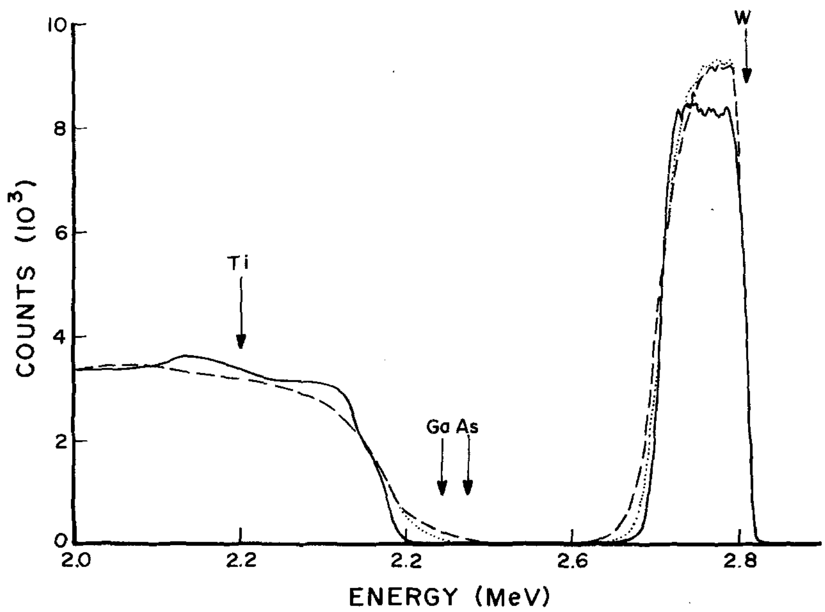


Figure 4 RBS spectra of (——) as-deposited, (···) 750 and (–––) 850° C annealed specimens. Annealing time 15 min.

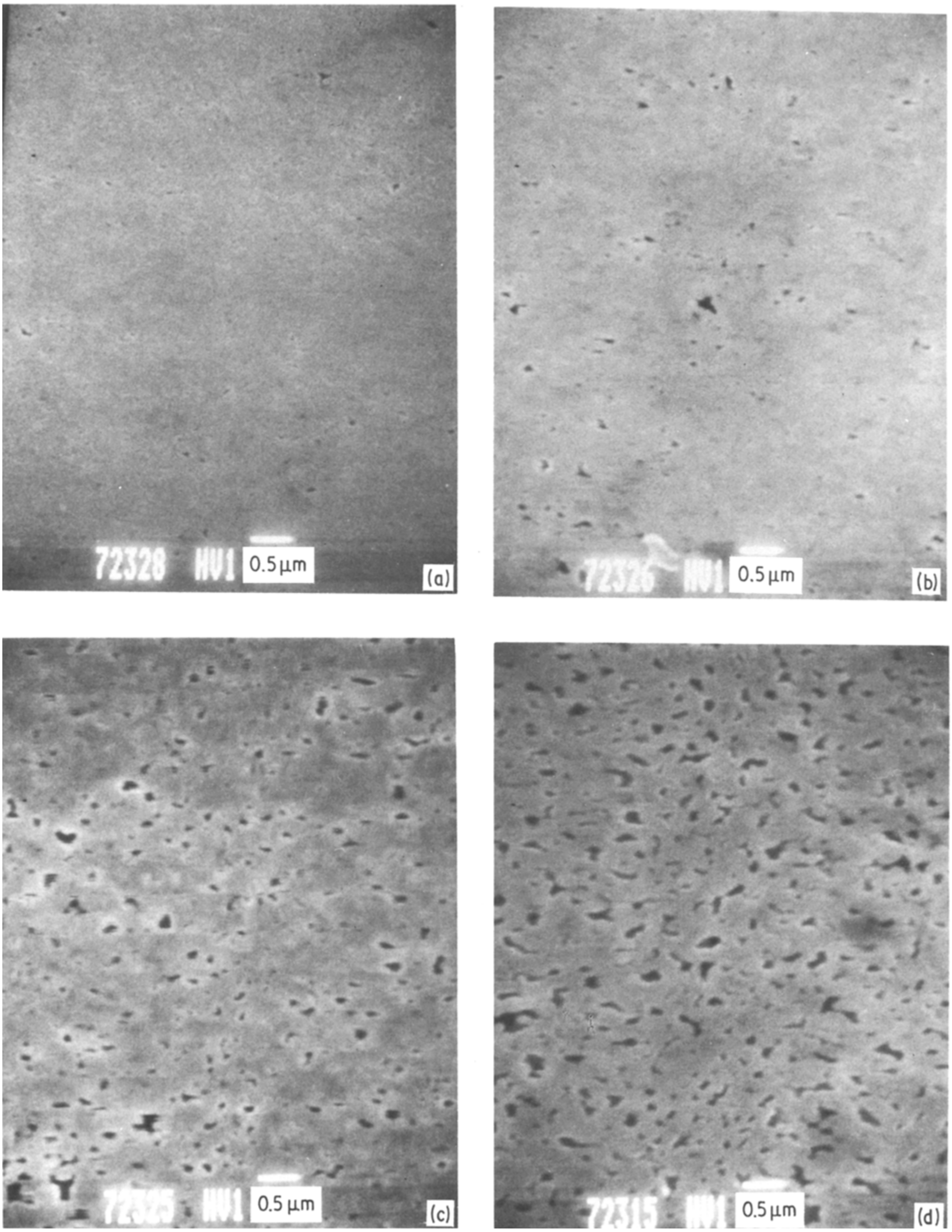


Figure 5 SEM micrographs of the surface of (a) 650, (b) 750, (c) 850 and (d) 900° C annealed specimens.

composition was found to be $Ti_{0.3}W_{0.7}$ and the thickness 100 nm. The heights of the tungsten signals of annealed samples are slightly higher than that of the as-deposited sample, indicating slight variations in thickness of the film in different regions of the wafer. The slopes at the lower-energy edge of the tungsten signal and the high-energy edge of the GaAs signal of annealed specimens decreased compared to that of signals of as-deposited film, indicating interfacial reaction with GaAs. The spectrum of the sample annealed at 650° C was similar to that of 750° C annealed specimen, and for clarity is not therefore shown in Fig. 4.

These observations are in agreement with TEM and X-ray diffraction results discussed earlier, where an AsTi compound was found to form at the interface starting at a temperature of 650° C. The arrows in Fig. 4 indicate the surface signals of tungsten, gallium, arsenic and titanium. It appears from the 750° C annealed spectrum that gallium has diffused through the TiW layer and reached almost up to the surface.

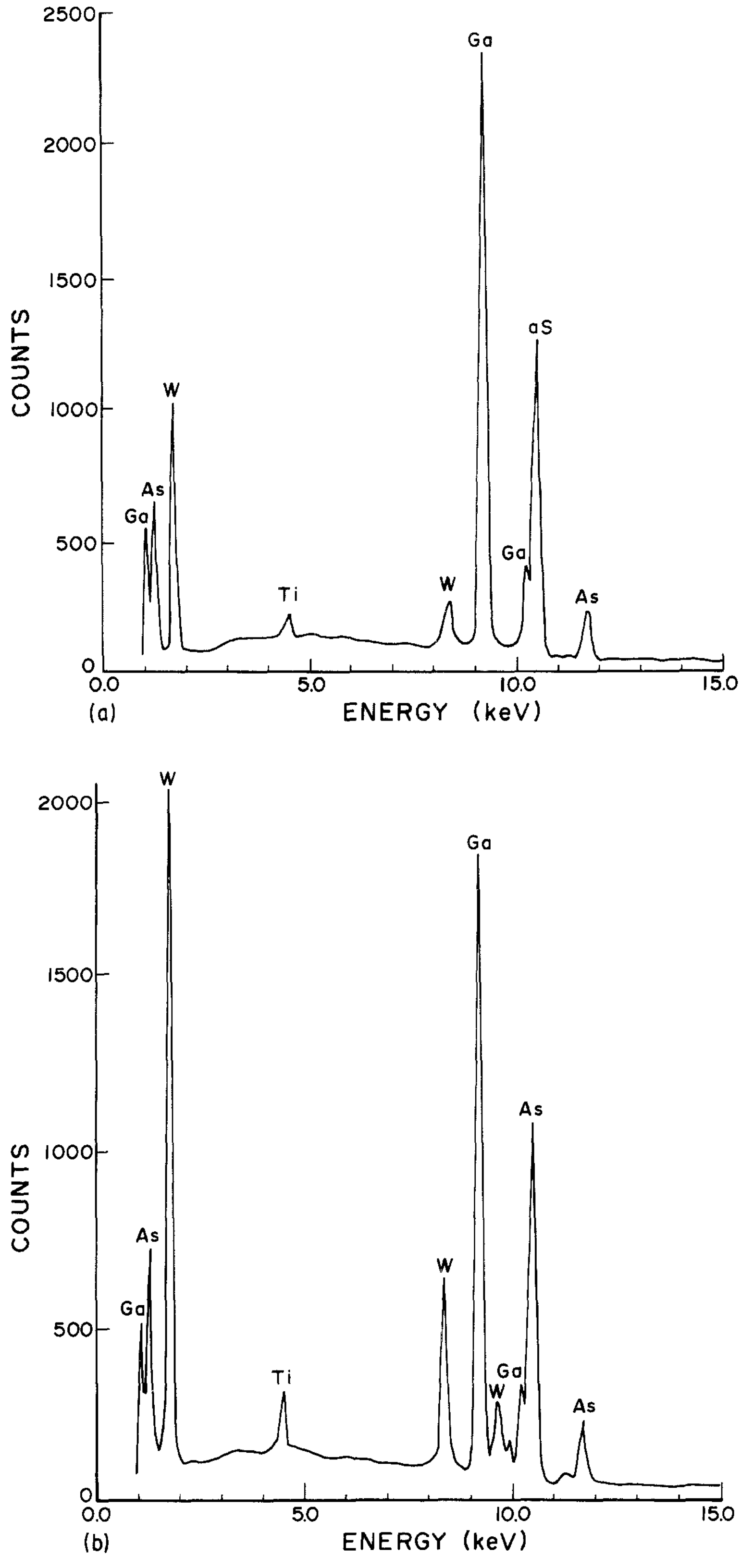


Figure 6 EDAX spectra of (a) black and (b) grey regions on the surface of 850° C annealed specimens.

Annealing at 850° C for 15 min has resulted in an increased interdiffusion. Some counts were recorded beyond the gallium surface signal, indicating that arsenic also diffused through the TiW layer at 850° C. Because of the low concentration and scattering cross-section of titanium, the step height due to titanium in the spectrum of the as-deposited sample is small but distinguishable which disappears after annealing, indicating inward diffusion. Employing RBS and secondary ion mass spectroscopy techniques, Yokoyama *et al.* [3] have shown that the reaction between TiW and GaAs takes place at 750° C and higher. In constrast, we could detect the occurence of reaction at a temperature as low as 650° C. This has been possible because of our use of detailed electron microscopy and higher energy (3 MeV He^+) RBS analysis.

The surface morphologies of the as-deposited and annealed TiW films were studied by scanning electron microscopy. The surface of the as-deposited film is found to be smooth. Figs. 5a, b, c and d represent the surface morphologies of the TiW film after annealing at 650, 750, 850 and 900° C, respectively. As is evident,

TABLE I Electron diffraction pattern analysis of TiW–GaAs interface region of 650° C annealed specimen

Some of the observed d values (nm)	Known d values of tungsten (nm)*	Known d values of AsTi (nm)†
0.279		0.2794
0.250		0.2479
0.224	0.2238	
0.217		0.2183
0.192		0.1919
0.182		0.1823
0.170		0.1693
0.156	0.1582	0.1559
0.129	0.1292	

*ASTM 4–0806.
†ASTM 7–134.

the surface smoothness deteriorated with the increase in annealing temperature. Black regions are found to be present in an otherwise grey background. The sizes and the density of these black regions are found to increase with annealing temperature. Figs. 6a and b represent the energy-dispersive X-ray spectra of the black and grey regions, respectively, of the 850° C annealed specimen. The black regions are found to be deficient in titanium and tungsten as compared to the grey regions. These observations show that the TiW film surface becomes non-uniform upon annealing at temperatures above 750° C.

4. Conclusions

The reactions of co-evaporated TiW films with GaAs have been studied after annealing at temperatures in the range of 650 to 900° C employing RBS, TEM, SEM, X-ray and EDAX techniques. It has been shown that titanium reacts with GaAs to form a hexagonal AsTi compound at temperatures as low as 650° C. It has been found from cross-sectional electron microscopy that the reaction between TiW film and GaAs does not take place uniformly. Gallium and arsenic have been found to move outwards, while titanium diffuses in upon annealing. Deterioration of the TiW film surface and the reaction of titanium with GaAs upon annealing may affect the electrical characteristics of TiW Schottky contacts on GaAs.

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Received 7 November 1984
and accepted 4 July 1985