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# Properties of titanium nitride thin films deposited by rapid-thermal-low-pressure-metalorganic-chemical-vapor-deposition technique using tetrakis (dimethylamido) titanium precursor

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Titanium nitride ( $\text{TiN}_x$ ) thin films were deposited onto InP by means of the rapid-thermal-low-pressure-chemical-vapor-deposition (RT-LPMOCVD) technique, using the tetrakis (dimethylamido) titanium  $\text{Ti}(\text{NMe}_2)_4$  or DMATi complex as the precursor. Depositions were successfully carried out at temperatures below 550 °C, pressure range of 5–20 Torr and duration of 50 to 90 s, to give layer thicknesses up to 200 nm and growth rates in the range of 0.8 to 4.5 nm/s. These films had a stoichiometric structure and contained nitrogen and titanium in a ratio close to unity, but also contained a significant amount of carbon and oxygen. The elements were spread uniformly through the films, the nitrogen was Ti bounded, and the carbon was partially titanium bonded and organic bonded as well. The film resistivity was in the range of 400–800  $\mu\Omega \text{ cm}^{-2}$ ; the stress was always compressive, in the range of  $-0.5 \times 10^9$  to  $-2 \times 10^{10} \text{ dyne cm}^{-2}$ , and the film had a good morphology. These layers performed as an ohmic contact while deposited onto  $p\text{-In}_{0.53}\text{Ga}_{0.47}\text{As}$  material, ( $\text{Zn}$ -doped  $1.2 \times 10^{18} \text{ cm}^{-3}$ ), provided an excellent step coverage for high aspect ratio via holes and were deposited selectively onto the InP and based materials when using  $\text{SiO}_2$  mask. This represents the first report of  $\text{TiN}_x$  films deposited in a commercial RT-LPMOCVD reactor using the DMATi precursor.

## I. INTRODUCTION

Titanium nitride ( $\text{TiN}_x$ ) thin films are of great interest in coating metallurgy, semi-metal technology and micro-electronic applications.  $\text{TiN}_x$  films display an interesting combination of properties, such as optical properties which resemble those of gold, hardness greater than all elemental metals, and sapphire and almost as hard as diamond, a very high melting point (about 300 °C) which implies high stability and excellent diffusion barrier properties, an inert nature for most of the chemicals and solvents, and finally a good electrical conductivity, higher than other metals such as titanium.

For microelectronic applications the  $\text{TiN}_x$  films are most commonly used in Si-based large-scale integrated circuits (LSI) technology, where they perform as an excellent diffusion barrier between the titanium silicide layer adjacent to the Si substrate and the W ohmic contacts. This novel W/ $\text{TiN}_x$ /TiSi/Si structure was proposed to suppress rapid silicidation of the W layer, as a result of Si outdiffusion from the TiSi layer, at temperatures higher than 800 °C.<sup>1–4</sup>

$\text{TiN}_x$  thin films have also been used in TiN/Ti/Pt/Au heterostructure diffusion/bonding metallization for 0.5  $\mu\text{m}$  gates in GaAs/AlGaAs high electron mobility transistor HEMT devices,<sup>5</sup> and for generic applications in GaAs device technology both as Schottky and ohmic metallization schemes.<sup>6,7</sup>

$\text{TiN}_x$  films may be deposited by reactive sputtering of titanium in an Ar– $\text{N}_2$  ambient,<sup>8–12</sup> by evaporation of titanium in the presence of  $\text{N}_2$ , followed by a 700–900 °C

inert gas annealing,<sup>13</sup> reduction of  $\text{TiSi}_2$  layer by  $\text{NH}_3$  at 900 °C,<sup>14</sup> and by the chemical vapor deposition (CVD) technique, either at atmospheric pressure (APCVD)<sup>15</sup> or at low pressure (LPCVD).<sup>16–19</sup>

The latter technique, which was introduced during the last two years, is of great interest in conjunction with III-V compound semiconductor technology, due to the sensitivity of these materials to surface degradation associated with ion beam deposition processes. Thus, while processing III-V materials, and in particular, those which include the more volatile group V elements, such as GaAs and InP, the various ion bombardment  $\text{TiN}_x$  deposition techniques are not appropriate.

The LPCVD  $\text{TiN}_x$  films were deposited with titanium tetrachloride ( $\text{TiCl}_4$ ) and ammonia ( $\text{NH}_3$ ) as the reactants in the temperature range of 450–700 °C and pressure range of 100–300 mTorr, at deposition rates of up to 100 nm/min. The electrical resistivity of the films varied in the range 50 to 100  $\mu\Omega \text{ cm}$ , depending solely on the amounts of carbon and oxygen that were entrapped in the layers. The films were typically stable at post-deposition annealing temperatures up to 550 °C. However, since chlorine chemistry is widely used as an etching technique for InP and related materials, the use of it for layer growth on InP should be avoided.

Recently Fix<sup>20,21</sup> have demonstrated deposition of  $\text{TiN}_x$  films using the earlier reported<sup>22–25</sup> volatile tetrakis (dialkylamido) titanium (IV) complex as a liquid metalorganic precursor. Two of these compounds, the dimethylamido titanium ( $\text{Ti}(\text{NMe}_2)_4$ ) and dimethylamido tita-

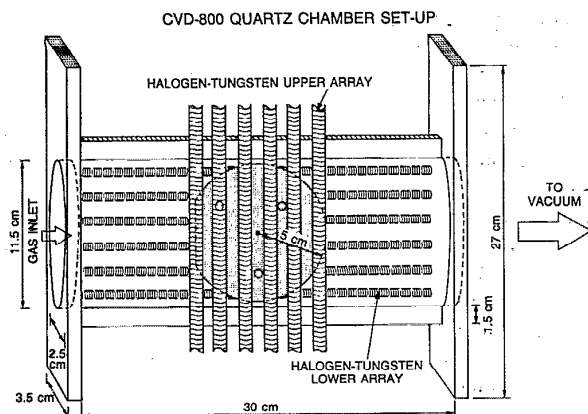


FIG. 1. Schematic representation of the reacting RT-LPMOCVD chamber.

nium ( $\text{Ti}(\text{NET}_2)_4$ ), have been used to deposit films of  $\text{TiN}_x$  at temperatures as low as 300 °C. These films had a stoichiometric Ti and N composition, but were heavily contaminated with oxygen and carbon. They have successfully demonstrated deposition onto glass, silicon, vitreous carbon, and boron substrates.

The purpose of this work is to implement the recent suggested tetrakis (DMATi) titanium metalorganic chemical vapor deposition (MOCVD) precursor for exploring deposition of  $\text{TiN}_x$  films onto InP and related materials by means of a cold wall, horizontal flow, rapid-thermal-low-pressure-chemical vapor deposition (RT-LPMOCVD) reactor. This is the first reported attempt at MOCVD deposition of  $\text{TiN}_x$  films onto InP, and in particular by means of RT-LPMOCVD technique.

## II. EXPERIMENT

The deposition of  $\text{TiN}_x$  films was carried out in a prototype of the now commercially available Heatpulse CVD-800™ system, designed in a joint effort between one of us<sup>26</sup> and A. G. Associates, a RTP equipment vendor. This is a low-pressure, horizontal and laminar flow oval cross-sectioned reactor that has two sets (upper and lower) of high-power halogen-tungsten lamps (12 lamps of 1.5 kW each) on both sides of a chamber which is capable of single-wafer processing with inert, hazardous, or corrosive ambients. This reactor has been previously described in detail elsewhere.<sup>27,28</sup> An overall schematic of the CVD-800™ reaction chamber is shown in Fig. 1 in which all the actual dimensions are inserted.

The  $\text{TiN}_x$  precursor was an American Cyanamid Tetrakis (dimethylamido) titanium (DMATi) Cypure™ product, loaded in a standard 100-g stainless-steel bubbler. This material, earlier synthesized by other groups as well,<sup>29,30</sup> has the molecular formula of  $\text{C}_2\text{H}_{24}\text{N}_4\text{Ti}$   $\{[(\text{CH}_3)_2\text{N}]_4\text{Ti}\}$ , molecular weight of 224.2, and boiling point of 50 °C at atmospheric pressure. Its density is unknown, while its vapor pressure as a function of temperature is given in Fig. 2. This compound has a very low vapor

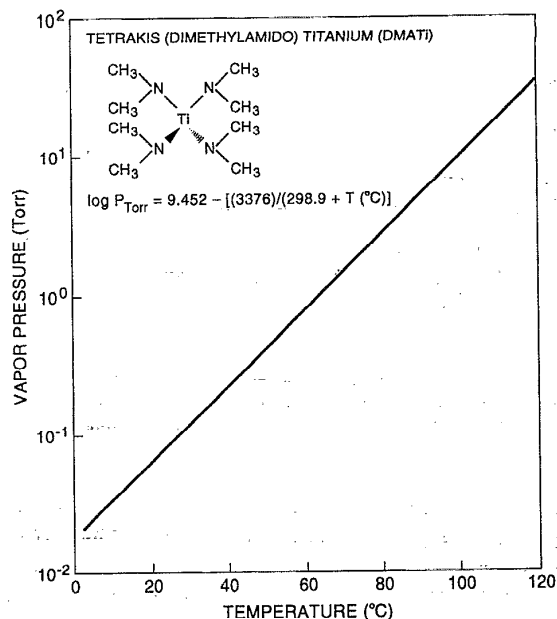


FIG. 2. Tetrakis (dimethylamido) titanium vapor pressure as a function of the liquid precursor temperature.

pressure of, for example, only 10 Torr at 100 °C, and is a viscous yellow liquid which decomposes upon exposure to water, air, and moisture. The chemical, physical, and toxicological properties of this material have not been fully investigated. Its handling and use are considered to be hazardous and requires some care. The decomposition temperature of the compound is in the range of 350 to 450 °C.<sup>31</sup>

Due to the low vapor pressure of DMATi ultrahigh-purity  $\text{H}_2$  flowed through a Nanochem gas purifier was used as a carrier gas. The RT-LPMOCVD chamber was kept always dry and clean due to the use of load-locked and gate-valve arrangements in the reactor. The chamber, after the loading of the sample, was pumped for 2 min, achieving a background pressure of  $5 \times 10^{-6}$  Torr. Subsequently the combined DMATi and  $\text{H}_2$  gas mixture was injected into the chamber, and the pressure stabilized before turning the lamps on. Figure 3 shows a typical  $\text{TiN}_x$  film deposition cycle plot which summarizes the various deposition conditions, such as the temperature (as was read by the pyrometer), total chamber pressure, and the conditions of each of the mass flow controllers (MFCs) through the various deposition steps, as a function of the process duration. The pressure, selected from different values in the range of  $5 \times 10^{-3}$ –50 Torr, was stable to an accuracy of  $\pm 1\%$  during the deposition cycle, which were performed at substrate temperatures in the range 320–520 °C, with an accuracy of  $\pm 10$  °C durations of 30–600 s, and flow rates in the range of 100–500 sccm.

The  $\text{TiN}_x$  films were deposited onto semi-insulating (SI)  $\langle 100 \rangle$ , 275- $\mu\text{m}$ -thick, 50-mm-diam InP wafers. On some wafers a  $p^+-\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$  (Zn doped,  $1.2 \times 10^{18} \text{ cm}^{-3}$ ) layer (0.5  $\mu\text{m}$  thick) was grown by

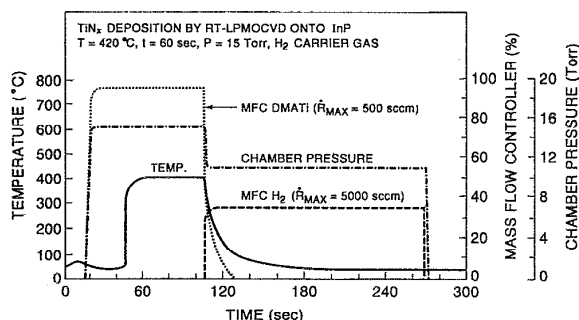


FIG. 3. RT-LPMOCVD process parameter plot. The plot provides the temperature, total chamber pressure and condition of the H<sub>2</sub> and DMATi mass flow controller, as a function of the TiN<sub>x</sub> deposition time.

MOCVD in order to allow for evaluation of the electrical properties of TiN<sub>x</sub> contacts to this material. The wafers were deoxidized in 10:1 H<sub>2</sub>O:HF solution and subsequently degreased by being rinsed in warm chloroform, acetone, and methanol. The wafers were loaded immediately after the cleaning procedure into the CVD-800™ load-lock chamber, which was then pumped down to a pressure of  $8 \times 10^{-5}$  Torr in a matter of 15 s.

InP substrates on which SiO<sub>2</sub> masking layers (300 nm thick) were deposited previously by RT-LPCVD<sup>27</sup> were also loaded into the chamber in order to investigate the selectivity of the TiN<sub>x</sub> deposition process.

For the electrical measurements using the transmission line method (TLM), the TiN<sub>x</sub> films were deposited onto linearly spaced (with intervals of 10–50 μm) square openings (200×200 μm<sup>2</sup>) that were wet-etched through a RT-LPCVD SiO<sub>2</sub> layer (300 nm thick). Subsequently, semiconductor mesas were wet-etched to give the required one-dimensional current flow.

Portions of the metal-deposited structures were rapid thermally processed (RTP) at temperatures of 300–550 °C in N<sub>2</sub> ambient at a pressure of 4–5 Torr and at a gas flow rate of 1500 sccm, subsequent to the TiN<sub>x</sub> RT-LPMOCVD, in order to investigate the electrical properties of the sintered TiN/*p*-InGaAs contacts.

Several analytical techniques were used to characterize the properties of the RT-LPMOCVD TiN<sub>x</sub> films and of the TiN<sub>x</sub>/InP and TiN<sub>x</sub>/*p*-InGaAs contact structure. Morphology and film thickness were studied by regular and high-resolution scanning electron microscopy (SEM) and transmission electron microscopy (TEM), in both cross-sectional and plan-view modes. Auger electron spectroscopy (AES) with sputter depth profiling was done using a PHI-S90 AES system to determine the stoichiometry of the TiN<sub>x</sub> layer, and the composition of metal-semiconductor interfaces. All the atomic elements involved in the deposited films were analyzed by secondary-ion mass spectrometry (SIMS). The SIMS analysis was done on a CAMECA IMS-4F model using a Cs<sup>+</sup> primary beam and detecting negative secondary ions. The depth scale was calibrated by measuring the depth of sputtered craters created by depth profiling. X-ray photoelectron spectroscopy (XPS) was

used, as well, to determine the actual film structure and the nature of the chemical element bonding.

Stress measurements were performed using the Flexus 2-300S thin-film stress measurement system. The substrates were measured for their initial curvature prior to any deposition or heat treatment. The initial curvature was subtracted from all the subsequent curvature measurements of the corresponding wafers after the RT-LPMOCVD was completed and after any further heat treatment of the deposited films. This technique has been described in detail previously.<sup>32</sup>

Deposited film thicknesses were measured using a Dektak™ stylus profilometry system. The variations ( $\Delta$ ) of the film thickness ( $x$ ) across the various wafers were defined as the following:

$$\Delta(\pm\%) = 100 \times (X_{\max} - X_{\min}) / (X_{\max} + X_{\min}).$$

The four-point probing technique was used to measure the sheet resistance of the deposited films.

Dry etching of the RT-LPMOCVD TiN<sub>x</sub> films was carried out in the following way: full area TiN<sub>x</sub> layers on top of InP substrates were patterned with AZ1330J photoresist in a test pattern containing a variety of openings of size in the range of 1–50 μm. The TiN<sub>x</sub> was etched in a pure SF<sub>6</sub> discharge contained within a hybrid electron cyclotron resonance (ECR)/radio frequency (rf) system.<sup>33</sup> The plasma pressure was varied in the range of 1 to 35 mTorr, the SF<sub>6</sub> flow rate was held constant at 30 sccm, and the microwave power was fixed at 150 W.

### III. RESULTS AND DISCUSSION

#### A. TiN<sub>x</sub> deposition kinetics and uniformity

An attempt was made to identify the influence of each of the RT-LPMOCVD process parameters, namely deposition temperature, pressure and temperature, on the TiN<sub>x</sub> film deposition rate. The growth rates were calculated from the thickness of the deposited layers, measured by both SEM and stylus profilometry. Five sets of samples were evaluated to investigate the appropriate deposition temperatures, in the range of 320–520 °C in intervals of 50 °C. Each set of samples was evaluated for deposition durations of 30 to 180 s in intervals of 10 s, controlled within  $\pm 1$  s, and over a wide pressure range. The latter was first examined in the range of  $5 \times 10^{-3}$ –50 Torr, and then the range was narrowed to the range of 5–35 Torr, which yielded the deposition of an acceptable TiN<sub>x</sub> material.

In an initial experiment it was found that the DMATi liquid precursor vapors had to be carried into the reaction chamber by a carrier gas due to its low vapor pressure, and thus ultra-purified H<sub>2</sub> at a flow rate of 1000 sccm was flown through the metalorganic source bubbler as a carrier gas. In addition the bubbler and gas lines were held at a temperature of 80 °C during all the experiments. This was the highest available temperature that did not create an unacceptably high humidity condition in the CVD-800™ gas handling module.

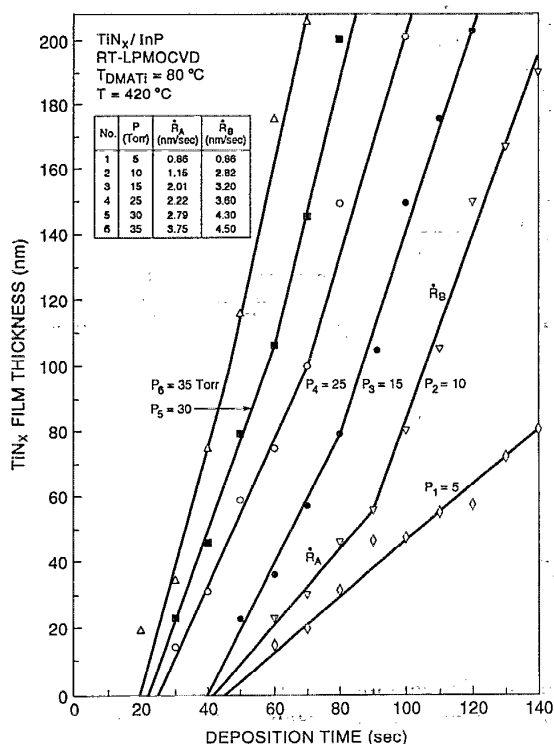


FIG. 4.  $\text{TiN}_x$  film thickness on InP substrates as a function of deposition duration at various chamber total pressure values.

The first correlation was drawn between the deposition temperature and the film growth rate. A temperature of  $420^\circ\text{C}$  was found to provide the most controlled and reproducible deposition conditions, and thus was held as the constant through the  $\text{TiN}_x$  RT-LPMOCVD evaluation study.

All the films deposited on 2 in. in diameter InP wafers were evaluated for film thickness uniformity. The results that are discussed in this work refer to deposition conditions that provided a  $\text{TiN}_x$  film thickness uniformity within a deviation of  $\pm 5\%$  across at least 80% of the wafers.

Figure 4 shows the variation of the  $\text{TiN}_x$  deposited film thickness at six different chamber pressures in the range of 5–35 Torr, as a function of the deposition duration at  $420^\circ\text{C}$ , while the DMATi bubbler was held at  $80^\circ\text{C}$ . These rates were calculated based on very intensive mechanical and cross-sectional SEM thickness measurements. A clear dependence of the growth rate on the deposition pressure is observed. In addition, one can observe the existence of a nucleation period for the initial  $\text{TiN}_x$  deposition to occur, getting shorter from 45 to 20 s, while increasing the chamber pressure from 5 to 35 Torr. At deposition pressures of 10 Torr or higher, two different deposition kinetics regimes were observed, both of which were linear in all the selected pressures. Figure 5 gives the dependence of the  $\text{TiN}_x$  film deposition rates on the total chamber pressure in the two regimes. The first region, apparent for short deposition durations, yielded deposition rates in the range of 0.86 to 3.75

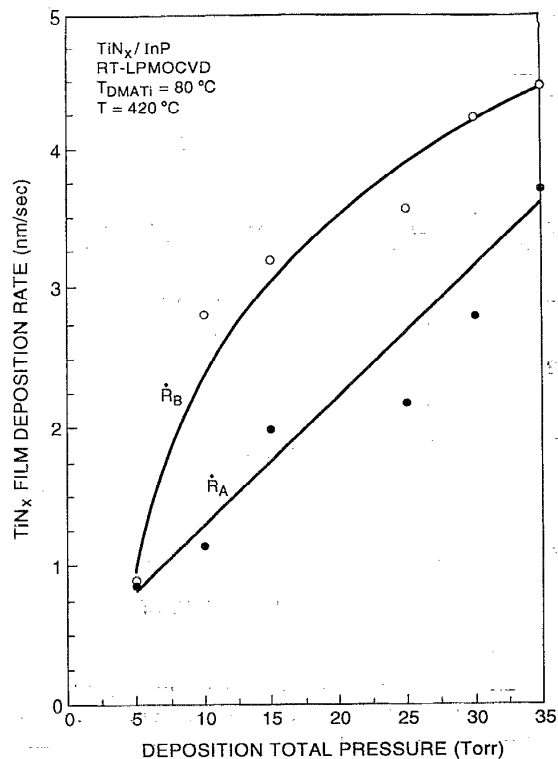


FIG. 5.  $\text{TiN}_x$  film deposition rates on InP substrates as a function of the chamber total pressure, for the two kinetic regions observed in the figure.

nm/s, while the second, apparent at longer deposition durations, varied between 0.86 and 4.50 nm/s. The most significant difference between the two regions was observed for the deposition pressure of 10–25 Torr. A further difference between the two kinetic regimes is observed in Fig. 5, which correlates the deposition rates and the total pressure. The first regime ( $R_A$ ), which reflects the shorter deposition duration associated with deposited film thickness of 55 to 100 nm shows a linear behavior with a slope of about  $0.095 \text{ nm s}^{-1}/\text{Torr}$ . The second regime ( $R_B$ ), which reflects the longer depositions durations, exhibits a parabolic dependence, suggesting some inhibition which increases with increasing the total process pressure. The reasons for the existence of these two regions are yet to be investigated, but the fact is that the  $\text{TiN}_x$  RT-LPMOCVD process at the pressure range of 10–25 Torr is most dependent on the process duration, as is reflected by the difference between ( $R_B$ ) and ( $R_A$ ) at these pressures.

## B. Film stoichiometry and impurities incorporation

AES and XPS depth profile data for the  $\text{TiN}_x$  films were obtained in order to determine the light-element incorporation and chemical bonding. Figure 6 gives AES surface scans of  $\text{TiN}_x$  films that were deposited under three different pressure conditions of  $3 \times 10^{-3}$  Torr [Fig. 6(a)], 1 Torr [Fig. 6(b)], and 15 Torr [Fig. 6(c)]. Chemical compositions for some representative films are given in Table I.

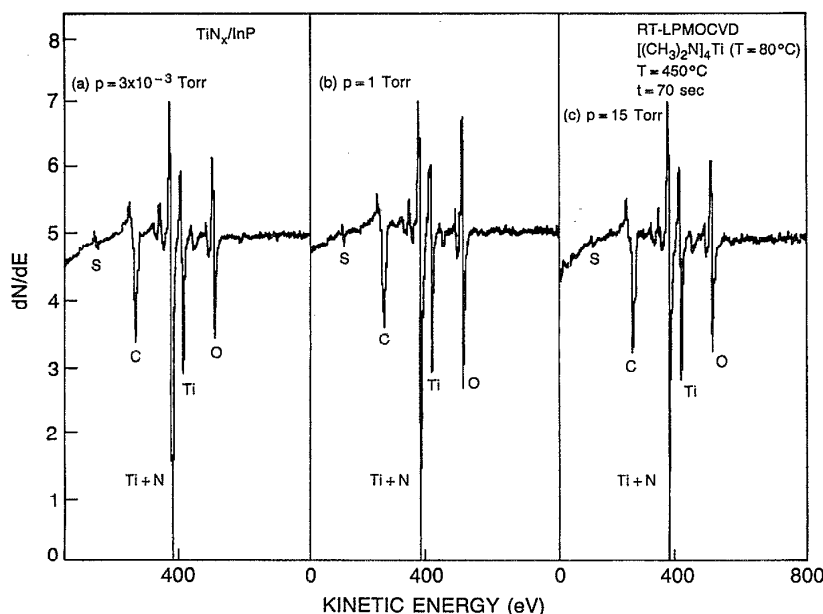


FIG. 6. AES surface survey of  $\text{TiN}_x$  film deposited onto InP substrates at a pressure of (a)  $3 \times 10^{-3}$  Torr, (b) 1 Torr, and (c) 15 Torr.

The data give the compositions of six films deposited at two different pressures of 12 and 25 Torr, and at each of these pressures using three different deposition temperatures of 420, 450, and 470 °C. All films contain a high concentration of carbon, which decreases with increasing the pressure, and oxygen, which exhibits the opposite trend. The nitrogen-to-titanium ratios varies from 1.1, for deposition at 12 Torr to 0.6 for deposition at 25 Torr. In both sets of samples the film composition is not dependent on the deposition temperatures. These results are in full agreement with the chemical composition of  $\text{TiN}_x$  films which were deposited by Fix *et al.*<sup>21</sup> using the same precursor, and are similar to those previously reported by Sugiyama.<sup>22</sup>

The stoichiometry of the  $\text{TiN}_x$  film was found to be constant through the layer, regardless of the deposition pressure, as is reflected in the AES profiles given in Fig. 7 for films that were deposited at total pressures of 12 Torr [Fig. 7(a)] or  $1 \times 10^{-3}$  Torr [Fig. 7(b)].

AES scans which were taken from the films verified the fact that the composition did not vary appreciably with depth. For example, Fig. 8 exhibits the surface scan [Fig. 8(a)] that was taken after three min of sputtering [Fig.

8(b)] on a  $\text{TiN}_x$  film that was deposited at a pressure of 12 Torr. Both scans are indistinguishable within the AES resolution limits.

The constant stoichiometry of the  $\text{TiN}_x$  films was observed as well by means of SIMS depth profiles, such as shown in Fig. 9 for a film that was deposited at 420 °C at a pressure of 10 Torr. Thus, one can conclude that the data presented in Table I are truly representative of the bulk compositions of the films.

### C. Light-element bonding

XPS analysis allowed for the identification of the light-element bonding configurations and some speculations with regard to the films chemical structure.

Figure 10 gives the XPS spectra after 3 min and 6 min of sputtering of  $\text{TiN}_x$  film. Three main peaks are of special interest, providing information about the nature of the incorporated light elements. Those are the carbon (1s) peaks (282 and 284.6 eV), the nitrogen (1s) peak (396.9 eV), and the Ti (2p) peak (454.8 eV). The carbon and titanium peaks at 282 and 454.8 eV, respectively, reflect many possible Ti—C bonding configurations, such as carbide

TABLE I. AES and XPS data for films deposited from tetrakis (dimethylamido) titanium (DMATi) precursor<sup>a</sup> onto InP.

| Deposition conditions |                 | at. % Composition (%) |    |    |    |      | Ratio |      |     |
|-----------------------|-----------------|-----------------------|----|----|----|------|-------|------|-----|
| Temp (°C)             | Pressure (Torr) | Ti                    | N  | O  | C  | N/Ti | O/Ti  | C/Ti | C/N |
| 420                   | 12              | 28                    | 31 | 6  | 35 | 1.1  | 0.2   | 1.2  | 1.1 |
| 450                   | 12              | 27                    | 31 | 7  | 35 | 1.1  | 0.2   | 1.3  | 1.1 |
| 470                   | 12              | 28                    | 30 | 8  | 36 | 1.1  | 0.3   | 1.2  | 1.1 |
| 420                   | 25              | 38                    | 22 | 13 | 27 | 0.6  | 0.3   | 0.7  | 1.2 |
| 450                   | 25              | 38                    | 22 | 14 | 26 | 0.6  | 0.3   | 0.7  | 1.2 |
| 470                   | 25              | 37                    | 21 | 15 | 27 | 0.6  | 0.4   | 0.7  | 1.2 |

<sup>a</sup>Precursor bubbler held at 80 °C.

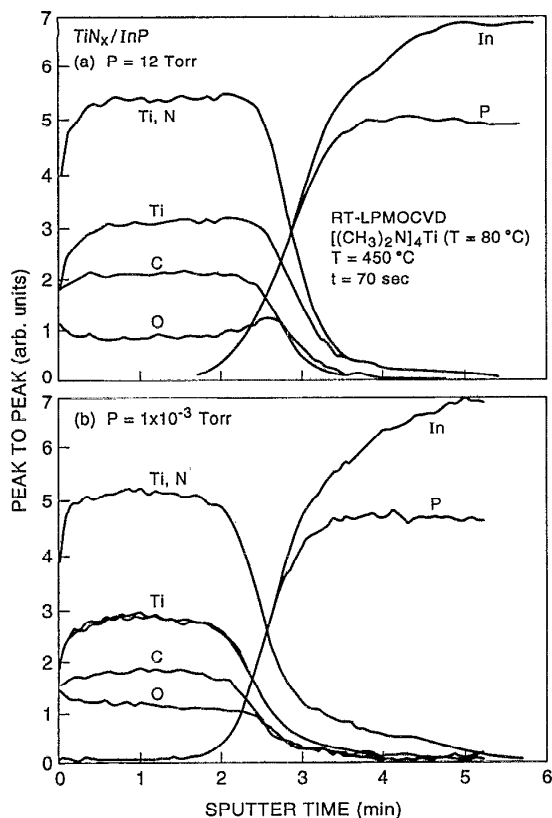


FIG. 7. AES depth profiles of  $\text{TiN}_x$  films deposited onto InP substrates under pressure of (a) 12 Torr, (b)  $1 \times 10^{-3}$  Torr.

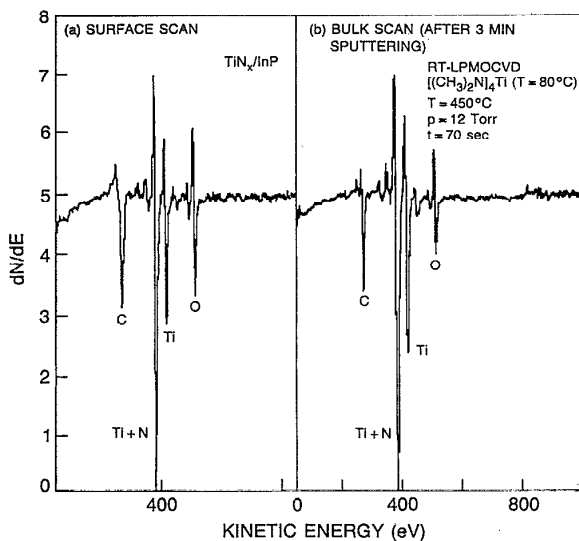


FIG. 8. AES survey of  $\text{TiN}_x$  film (a) surface, and (b) bulk, after 3-min sputtering.

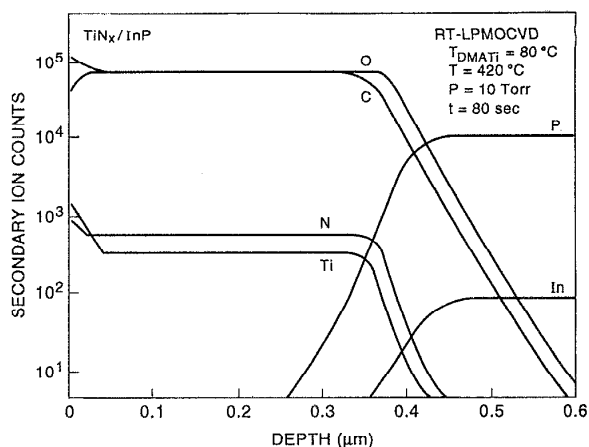


FIG. 9. SIMS depth profile of  $\text{TiN}_x$  film deposited onto InP substrate.

(Ti—C),  $\text{Ti}=\text{CH}-$ , or  $-\text{Ti}-\text{CH}_2$  groups.<sup>21,34,35</sup> The secondary carbon peak at 284.6 represents the carbon incorporated into organic groups, whether attached to other carbon, or nitrogen or oxygen. The nitrogen peak at 396.9 eV reflects nitrogen incorporated in the nitride (Ti—N) form. Some other combinations of ternary bonded structures, containing these three elements are possible as well.

#### D. Film stress and resistivity

The sheet resistance, resistivity and stress of  $\text{TiN}_x$  films, were measured at room temperature for the RT-LPMOCVD as-deposited layers. The resistivity and stress values are given in Fig. 11 as a function of the total chamber pressure during the deposition. For the resistivity, an optimum value was found for the pressure range of 15 to 17 Torr which yielded a minimum value of about 425

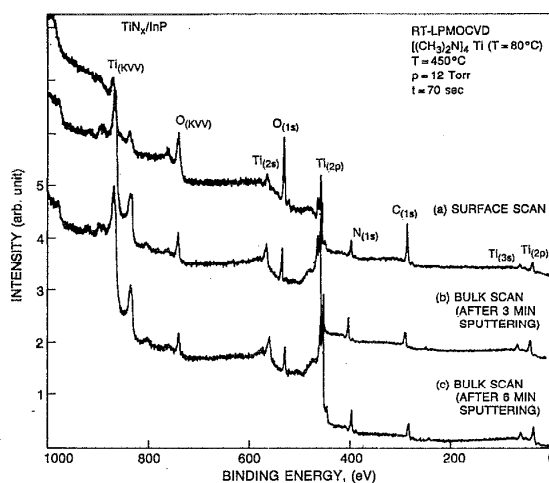


FIG. 10. XPS spectra of  $\text{TiN}_x$  film (a) surface, and bulk after (b) 3- and (c) 6-min sputtering.

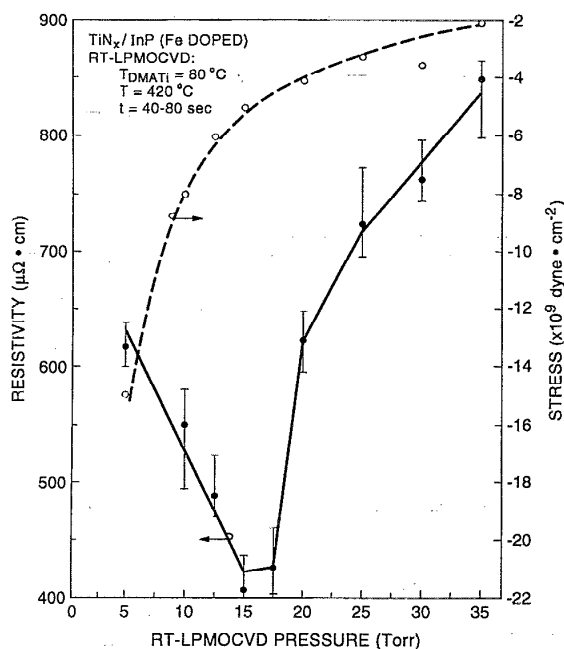


FIG. 11. Resistivity and stress of  $\text{TiN}_x$  films on SI-InP substrates as a function of the total chamber pressure.

$\mu\Omega \text{ cm}$ . This value is about three times higher than the value measured for pure Ti films ( $165 \mu\Omega \text{ cm}$ ),<sup>36</sup> due to the high concentration of C and O. Increasing the deposition pressure to higher values, up to 35 Torr, resulted in increase of the film resistivity values to over  $800 \mu\Omega \text{ cm}$ .

For the stress measurements, all the as-deposited RT-LPMOCVD  $\text{TiN}_x$  films displayed compressive stresses ranging from about  $-1.5 \times 10^{10} \text{ dyne cm}^{-2}$ , for deposition pressures of 5 Torr, to about  $-2 \times 10^9 \text{ dyne cm}^{-2}$ , for deposition at 35 Torr. Surprisingly, these values are very similar to the stress values that were measured for reactive sputter deposited  $\text{TiN}_x$  films.<sup>37</sup>

Stress measurements were performed while heating the as-deposited  $\text{TiN}_x$  films to  $500^\circ\text{C}$  and cooling them back to room temperature, both at rates of  $10^\circ\text{C}/\text{min}$ . Figure 12 shows the  $\sigma$ - $T$  plots of three different  $\text{TiN}_x/\text{InP}$  samples as representatives of a much wider set of experiments. Those films were deposited at a temperature of  $420^\circ\text{C}$  for durations of 40–80 s under total pressures of 5, 12, and 25 Torr. All the samples as-deposited were under compressive

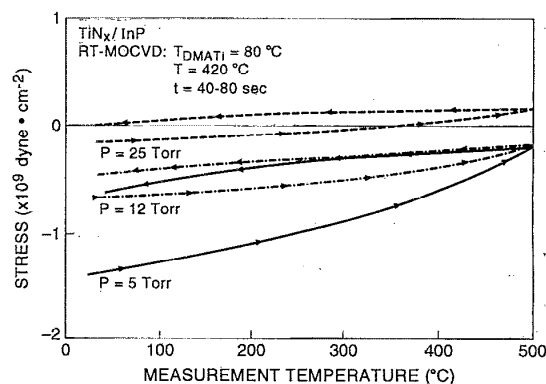


FIG. 12. Stress as a function of the  $\text{TiN}_x$  film measuring temperature.

stresses of  $-1.5 \times 10^{10}$ ,  $-2.5 \times 10^9$ , and  $-8 \times 10^8 \text{ dyne cm}^{-2}$ , respectively, and developed some kind of plastic deformation through the heating cycles, as is reflected by the hysteresis of the  $\sigma$ - $T$  graphs. The higher the deposition pressure the smaller the plastic deformation due to the heat treatment. This suggests a change in the film morphology and density influenced by modification of the deposition pressure.

### E. Morphology

Figure 13 shows SEM high-resolution micrographs of  $\text{TiN}_x$  films that were deposited on InP at a temperature of  $420^\circ\text{C}$  and pressure of 15 Torr for durations of 100 s [Fig. 13(a)], 90 s [Fig. 13(b)], 70 s [Fig. 13(c)] and 60 s [Fig. 13(d)]. The excellent and defect-free morphology of the films is shown clearly at these micrographs and was observed, as well, in SEM plan-view samples. Another interesting observation is the abrupt  $\text{TiN}_x/\text{InP}$  interface, in spite of the relatively high RT-LPMOCVD deposition temperature. This phenomena will be mentioned again later in this paper when discussing the TEM results.

Lowering the deposition pressure to 5 Torr resulted in the growth of discontinuous and heavily damaged film that was grown at 5 Torr for 100 s exhibited a high density defected structure and suffered from a severe growth non-uniformity. Extending the growth duration to 180 s, resulted in a nominal layer thickness of 1800 nm, which allowed for an improved surface coverage, however exhibited the presence of large scale defects, and basically replicated the initial defected film coverage.

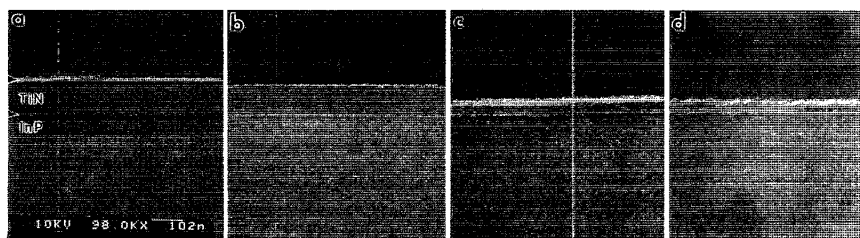


FIG. 13. High-resolution SEM cross-sectional micrographs of  $\text{TiN}_x$  films deposited onto InP substrates at chamber total pressure of 15 Torr and a temperature of  $420^\circ\text{C}$  for durations of (a) 100, (b) 90, (c) 70, and (d) 60 s.

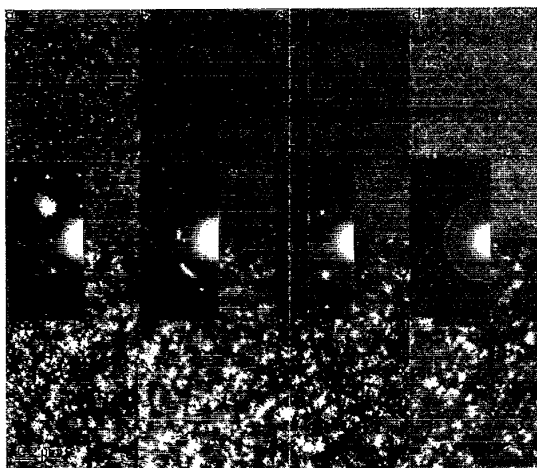


FIG. 14. TEM plan-view bright field (upper) and dark field (lower) micrographs, and the associated SAD patterns, of  $\text{TiN}_x$  films deposited onto InP substrates at temperature of 420 °C, and pressures of 10 Torr for (a) 80, and (b) 110 s, and pressure of 15 Torr for (a) 80 and (b) 110 s.

The above-mentioned SEM results provide a clear observation as to the quality of the  $\text{TiN}_x$  film morphology, suggesting that the lower pressure limit under which the RT-LPMOCVD process still yields acceptable material is 10 Torr.

#### F. Microstructure

Figure 14 shows TEM plan-view micrographs in both bright-field (upper micrographs) and dark-field (lower micrographs) modes, and the corresponding selected area diffraction (SAD) patterns of  $\text{TiN}_x/\text{InP}$  samples as-deposited at a temperature of 420 °C and pressures of 10 Torr, for 80 [Fig. 14(a)] and 110 s [Fig. 14(b)], and of 15 Torr for 80 [Fig. 14(c)] and 110 s [Fig. 14(d)]. All the films exhibit a polycrystalline structure with very fine grain size. The only phase that was identified by means of the SAD was TiN, which has a cubic structure and presents SAD ring radius values as shown in Fig. 15.<sup>38</sup>

Figure 16 shows the TEM cross-sectional micrographs of the  $\text{TiN}_x/\text{InP}$  samples that were RT-LPMOCVD at a temperature of 420 °C and pressures of 10 Torr for 110 s [Fig. 16(a) bright field, 16(b)-dark field], and 15 Torr for 80 s [Figs. 20(c) bright field, 20(d)-dark field]. From these micrographs one can conclude that the InP substrates did not suffer any degradation through the deposition of  $\text{TiN}_x$  films, and therefore the  $\text{TiN}_x/\text{InP}$  interfaces remained sharp, regardless of the variations in the total pressure and deposition durations.

#### G. Dry etching

The as-deposited RT-LPMOCVD  $\text{TiN}_x$  films were dry etched using a hybrid electron cyclotron resonance (ECR)/radio frequency (rf) reactor. The etch rate of the TiN in an  $\text{SF}_6$  discharge (30 sccm, -100-V dc bias, 150-W microwave power) was independent of the deposition

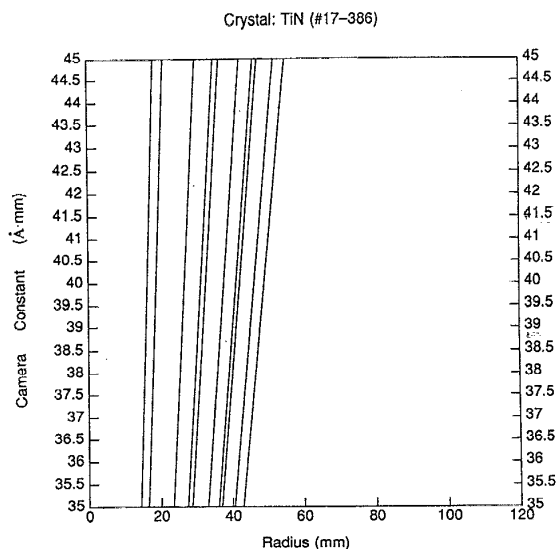


FIG. 15. TEM camera constant and the SAD ring radius of the  $\text{TiN}_x$  phase. (see Ref. 38).

pressure used for the film. This is quite different to the characteristics of  $\text{WSi}_x$  and  $\text{SiO}_2$  which we have examined earlier,<sup>27,28</sup> where we observed a pronounced dependence of dry etching rate on the deposition pressure. In the case of  $\text{TiN}_x$ , however, in spite of the stress dependence on the deposition pressure, there is no significant differences in the dry etching rates. Further experiments are contacted in attempt to understand this characteristic.

At fixed dc bias (-100 V) on the sample during the  $\text{SF}_6$  dry etching, we observed a rapid increase in the  $\text{TiN}_x$  etch rate for microwave powers above ~200 W. At these power levels the density of active fluorine species in the discharge increases, leading to faster TiN etch rates (Fig. 17). At this low bias value there is no damage intro-

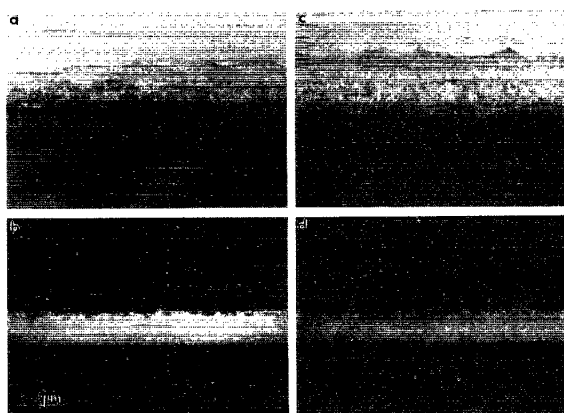


FIG. 16. TEM cross-sectional micrographs of  $\text{TiN}_x$  films deposited onto InP substrates at temperature of 420 °C and pressure of 10 Torr for 110 s, at the (a) bright-field and (b) TiN dark-field modes, and pressure of 15 Torr for 80 s, at the (c) bright field and (d) TiN dark-field mode.

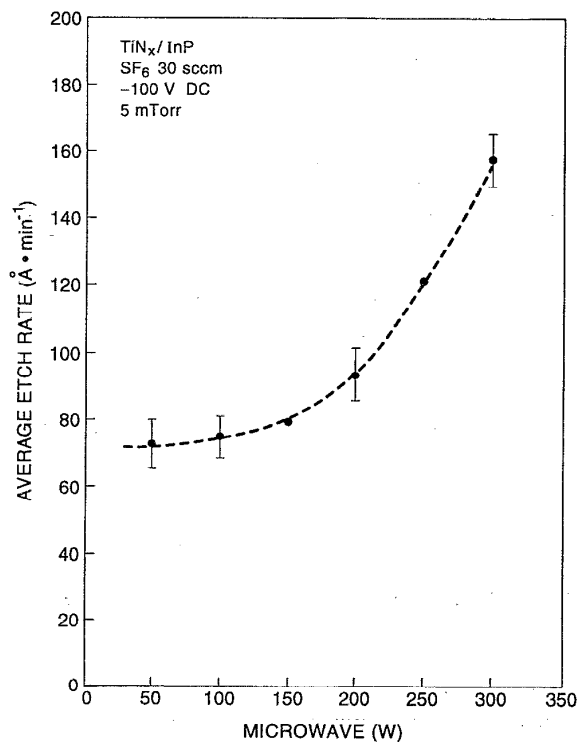


FIG. 17. ECR/RF etch rate of an RT-LPMOCVD TiN film deposited at temperature of 420 °C and pressure of 10 Torr, as a function of the microwave power at a constant SF pressure and dc bias.

duced into the underlying InP and TiN can be etched with infinite selectivity to the InP. This is an ideal situation with respect to using the TiN as a contact layer in device structures.

As the plasma pressure was increased from 1 to 20 mTorr at constant dc bias (–100 V) and microwave power level (150 W), we also observed an increase in the TiN etch rate, as shown in Fig. 18. We believe this is also a result of having a higher density of active fluorine species available for etching the TiN at higher pressures. There is a saturation behavior evident at the higher pressures as the etching is no longer reactant-limited.

Figure 19 shows micrographs of TiN<sub>x</sub> films, deposited onto InP substrates, that were ECR/RF dry etched through an AZ1350J photoresist patterned mask. The figure shows the efficiency of the etching process, patterning TiN features at micron size dimensions. It was found that the roughness of the etched feature edges, is due to the accurate replication of the photoresist mask on the InP and not due to some technical problems with the process itself.

#### H. Selective growth

Another task that was investigated is the selectivity of the TiN<sub>x</sub> RT-LPMOCVD process. The SEM photographs in Fig. 20 illustrate good selectivity of the deposition process onto InP masked by SiO<sub>2</sub> films. These structures were prepared in the following way: A combined structure of *p*-

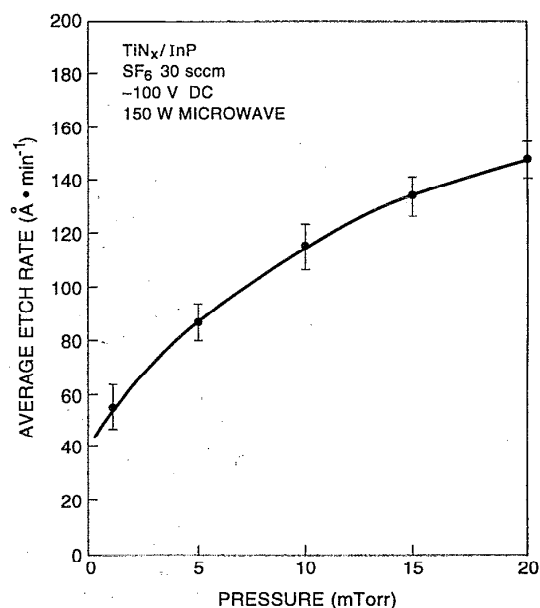


FIG. 18. ECR/RF etch rate of an RT-LPMOCVD TiN film deposited onto InP substrates at temperature of 420 °C and pressure of 10 Torr, as a function of the plasma pressure, at constant dc bias and microwave power.

In<sub>0.53</sub>Ga<sub>0.47</sub>As layer (0.5 μm thick) was epitaxially grown by means of MOCVD on semi-insulating (SI) InP substrates. Subsequently a SiO<sub>2</sub> layer (about 300 nm thick) was deposited onto the ternary layer by means of RT-LPVCD using diluted SiH<sub>4</sub> (2% in Ar) and O<sub>2</sub> as gas sources for the process, widely described elsewhere.<sup>27</sup> An intermediate photolithography process allowed for the definition of the patterned features (as is shown in Fig. 20) to be wet etched in the SiO<sub>2</sub> film. These structures were reloaded into the CVD-800M68 reactor and TiN<sub>x</sub> (50 nm thick) was then RT-LPMOCVD onto them at 420 °C using the DMATi liquid precursor vapor, carried into the chamber by ultrapurified H<sub>2</sub>.

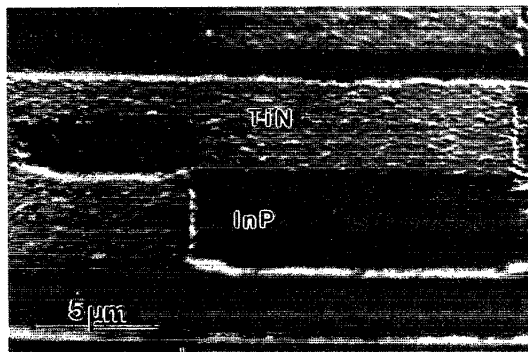


FIG. 19. SEM plan-view of ECR/RF etched features in a TiN<sub>x</sub> film, deposited onto an InP substrate at a temperature of 420 °C and pressure of 10 Torr.

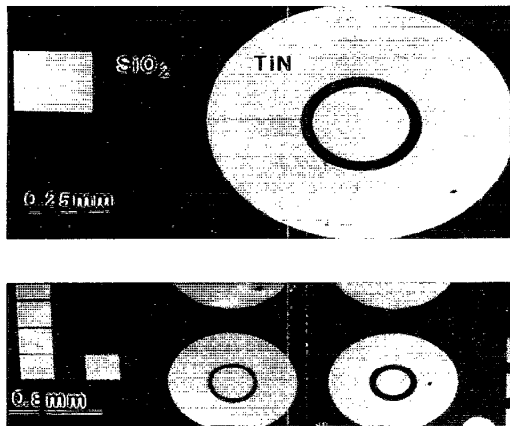


FIG. 20. SEM plan-view of selective area deposition of RT-LPMOCVD  $\text{TiN}_x$  films onto etched patterns in RT-LPCVD  $\text{SiO}_2$  layer over a  $p\text{-In}_{0.53}\text{Ga}_{0.47}\text{As}$  layer on top of a SI-InP substrate.

The  $\text{TiN}_x$  RT-LPMOCVD selectivity is demonstrated in Fig. 21. In this case we have purposely deposited a  $\text{TiN}_x$  film onto the patterned  $\text{SiO}_2$  layer, with both films having approximately the same thickness. This procedure serves as a severe test on the  $\text{TiN}_x$  selectivity by allowing a full coverage of the patterned features to exceed the height of the  $\text{SiO}_2$  layer and subsequently a growth of  $\text{TiN}_x$  over the  $\text{SiO}_2$ .

The selectivity mechanism of the RT-LPMOCVD  $\text{TiN}_x$  onto InP-based materials over RT-LPCVD  $\text{SiO}_2$ , is currently under further investigation.

### I. Electrical properties

As was discussed in the previous paragraph the  $\text{TiN}_x$  films were RT-LPMOCVD onto wet-etched patterns in the RT-LPCVD  $\text{SiO}_2$  layer, in a selective manner, capping a  $p\text{-In}_{0.53}\text{Ga}_{0.47}\text{As}$  (Zn doped  $1.2 \times 10^{18} \text{ cm}^{-3}$ ) epitaxial grown layer on a SI-InP substrate.

Figure 22 presents the TLM derived resistance measurements, taken in the patterns shown in Fig. 20, for the  $\text{TiN}_x$  contacts to the  $1.2 \times 10^{18} \text{ cm}^{-3}$  Zn-doped

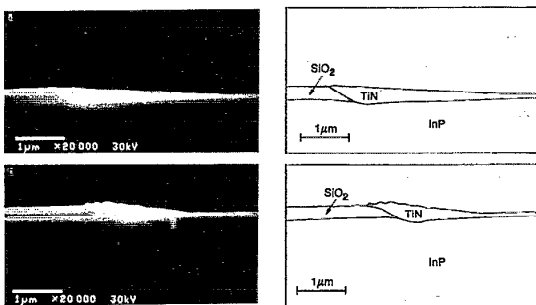


FIG. 21. SEM cross-sectional micrographs of a self-aligned  $\text{TiN}_x/\text{InP}$  stack deposited at  $420^\circ\text{C}$ , at pressures of (a) 15 and (b) 25 Torr.

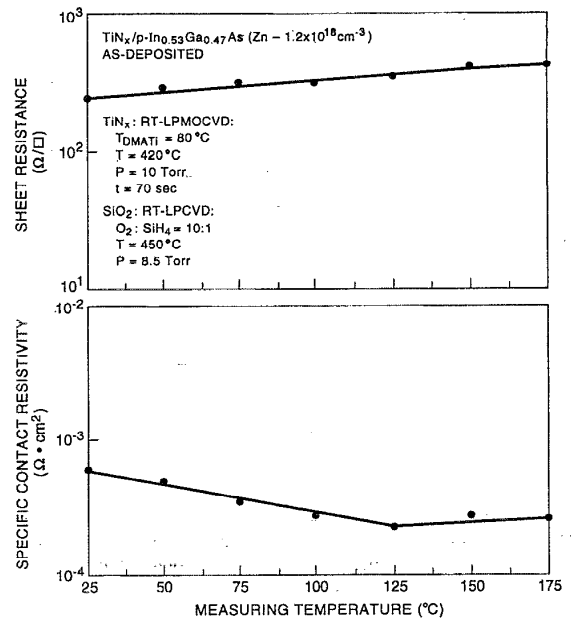


FIG. 22. (a) Sheet resistance and (b) specific contact resistivity as a function of the measuring temperature of  $\text{TiN}_x$  RT-LPMOCVD contacts on a  $p^+\text{-In}_{0.53}\text{Ga}_{0.47}\text{As}$  (Zn-doped  $1.2 \times 10^{18} \text{ cm}^{-3}$ ) layers.

$\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$  as deposited, when measured at room temperature and elevated temperatures up to  $175^\circ\text{C}$ . The plotted values were averaged over 30 points and were displaced standard deviations less than 35%. Figure 22(a) shows the sheet resistance ( $R_s$ ) at the different measuring temperatures, with a value that varies linearly from  $240 \Omega/\square$  measured at  $25^\circ\text{C}$ , to about  $420 \Omega/\square$  measured at  $175^\circ\text{C}$ . Figure 22(b) shows the specific contact resistivity values of the as-deposited  $\text{TiN}_x/p\text{-InGaAs}$  contacts measured over the temperature range of  $25\text{--}175^\circ\text{C}$ . These values were found to stay almost constant with negligible decrease from about  $6 \times 10^{-4}$  to about  $2 \times 10^{-4} \Omega \text{ cm}^2$  when measured at temperatures of  $150^\circ\text{C}$  and higher.

Table II provides the ideality values and the Schottky barrier heights of the  $\text{TiN}_x/p\text{-InGaAs}$  contacts as deposited as were measured at different temperatures in the

TABLE II. Ideality values ( $n$ ) and Schottky barrier heights ( $\phi_B$ ) of the  $\text{TiN}_x/p\text{-InGaAs}$  as-deposited contacts, measurement at various temperatures.

| No. | Temp. ( $^\circ\text{C}$ ) | Ideality ( $n$ ) | $\phi_B$ (eV) |
|-----|----------------------------|------------------|---------------|
| 1   | 20                         | 0.28             | 0.45          |
| 2   | 40                         | 0.24             | 0.44          |
| 3   | 60                         | 0.22             | 0.43          |
| 4   | 80                         | 0.18             | 0.40          |
| 5   | 100                        | 0.17             | 0.40          |
| 6   | 120                        | 0.16             | 0.39          |
| 7   | 140                        | 0.18             | 0.38          |
| 8   | 160                        | 0.26             | 0.32          |
| 9   | 180                        | 0.29             | 0.30          |

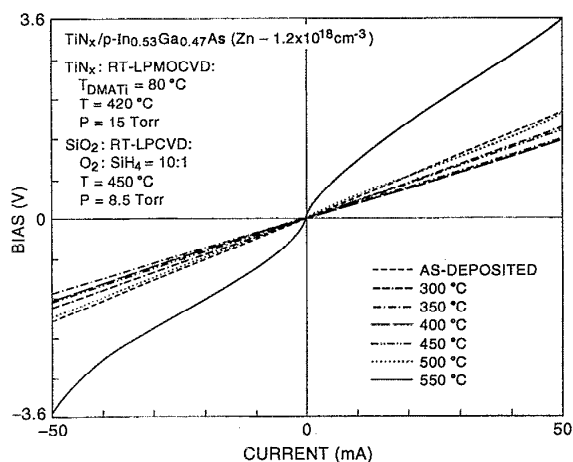


FIG. 23. Voltage-current characteristic of the as-deposited  $\text{TiN}_x$  RT-LPMOCVD on a  $p^+$ - $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$  (Zn-doped  $1.2 \times 10^{18} \text{ cm}^{-3}$ ) layer, and after RTP at low pressure (4.5 Torr)  $\text{N}_2$  at various temperatures.

range of 20–180 °C. A slight decrease of the Schottky barrier was observed upon elevating the measuring temperature, from 0.45 eV measured at 20 °C to 0.30 eV measured at 180 °C.

In an attempt to improve the electrical properties of the  $\text{TiN}_x/p\text{-InGaAs}$  contact, a post-deposition sintering heat treatment was applied to the contacts. Heat treatment at temperatures which varied in the range of 300–550 °C under a  $\text{N}_2$  ambient with a total pressure of about 4.5 Torr were applied to the contacts subsequent to the RT-LPMOCVD cycle of the  $\text{TiN}_x$  films.

Figure 23 shows the bias-current ( $V$ - $I$ ) characteristics of the  $\text{TiN}_x/p\text{-InGaAs}$  contacts. One can see that the as-deposited contact, and the contacts that were sintered at temperatures up to 500 °C exhibit a linear  $V$ - $I$  curves reflecting an ohmic nature. Heating the contact at 550 °C resulted in a clear degradation of the ohmic behavior and led to the transition to a rectifying contact.

Further investigation of the contact electrical characteristic suggested an improvement of about one order of magnitude in the specific contact resistivity, decreasing from about  $3.5 \times 10^{-4} \Omega \text{ cm}^2$  as-deposited, to about  $4 \times 10^{-5} \Omega \text{ cm}^2$ , as a result of the post-deposition sintering at 500 °C as is shown in Fig. 24.

#### IV. SUMMARY AND CONCLUSIONS

We have demonstrated the ability of the CVD-800™ to deposit  $\text{TiN}_x$  films onto InP substrates and  $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$  epitaxial layers, using the tetrakis (Dimethylamido) titanium metalorganic liquid precursor.

The influence of the process parameters on the deposition kinetics, film stoichiometry, impurity incorporations, morphology, and microstructure were intensively evaluated. For high quality films, deposition temperature window was found to be the range of 350–550 °C the total pressure in the chamber between 10 and 20 Torr, and deposition durations between 50 and 90 s. These conditions

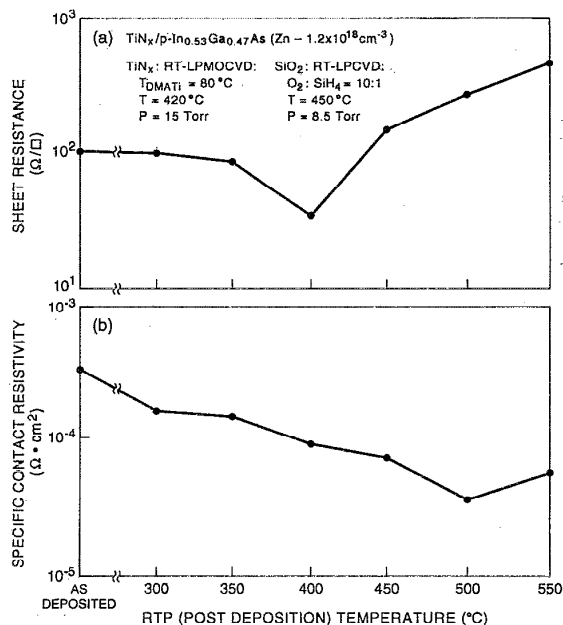


FIG. 24. (a) Sheet resistance and (b) specific contact resistivity of  $\text{TiN}_x$  RT-LPMOCVD on a  $p^+$ - $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$  (Zn-doped  $1.2 \times 10^{18} \text{ cm}^{-3}$ ) layer, as-deposited and after RTP at low pressure (4.5 Torr)  $\text{N}_2$  at various temperatures.

allowed for deposition rates of about 0.8 to 4.5 nm/s, mainly dependent on the substrate temperature and total pressure.

A Ti/N stoichiometric ratio of almost unity was achieved in the  $\text{TiN}_x$  films, however, we found an incorporation of high C and O concentrations of about 35% and 6%, respectively. These impurity levels are typical in  $\text{TiN}_x$  films deposited from amido and imido titanium (IV) compound precursors and further work is currently going on in an attempt to reduce these concentrations.

Stress measurements and dry etching rates provided encouraging data with regard to the high stability nature of these films, which had an initial, as-deposited compressive stress in the range of  $-5 \times 10^{18}$  to  $-1.5 \times 10^{10} \text{ dyne cm}^{-2}$ .

We have investigated the quality of the step-coverage of the process, which was found to be excellent and demonstrated the selectivity nature of the  $\text{TiN}_x$  RT-LPMOCVD onto InP over  $\text{SiO}_2$ .

Contacts that were prepared by RT-LPMOCVD of the  $\text{TiN}_x$  onto  $p^+$ - $\text{InGa}_{0.53}\text{Ga}_{0.47}\text{As}$  (Zn-doped  $1.2 \times 10^{18} \text{ cm}^{-3}$ ) performed with an ohmic nature, and exhibited a minimum specific contact resistivity of about  $3.5 \times 10^{-5} \Omega \text{ cm}^2$ , as a result of post-deposition sintering at 500 °C for 30 s under a low-pressure (4.5 Torr)  $\text{N}_2$  ambient.

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