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A parametric study of the deposition of the TiN thin films by laser reactive ablation of titanium targets in nitrogen: the roles of the total gas pressure and the contaminations with oxides

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The multipulse excimer laser-reactive ablation of a titanium target in nitrogen has been found to result in a total pressure of the ambient gas in the range 7–70 μbar, in the deposition on to a silicon collector surface of high-purity fcc TiN thin films. These films were hard and adherent to substrate. The deposition rate was 0.03–0.05 nm per pulse for an incident laser fluence of $\geq 5\ \mathrm{J\,cm^{-2}}$. For a lower gas pressure of a few microbars the deposits were amorphized with an excess of titanium. For a nitrogen pressure larger than 100 μbar, the layers were contaminated with oxides. The oxides became more abundant with further increase in the gas pressure, and the deposited layer consisted of oxides only when the pressure reached several millibars.

1. Introduction

Titanium nitride thin films exhibit a unique combination of high hardness, good chemical inertness, beautiful colour and excellent wear resistance. They are widely used as wear-resistant coatings and for surface decoration [1,2]. Recently they have been used in semiconductor devices [3,4], contact layers for solar cells [5] and as a replacement of polycrystalline silicon in very large-scale metal/oxide/semiconductor integrated (VLSI) circuits.

A number of techniques are currently available for the deposition of TiN films. TiN films prepared by reactive sputtering are used as diffusion barriers in metallization technology of silicon devices [1,5–9]. Coatings of TiN have commonly been deposited by various physical vapour deposition (PVD) and chemical vapour deposition (CVD) methods [10]. In particular, although successful in the deposition of TiN thin layers [10–17], these methods have some drawbacks:

(i) the sputtering/evaporation can be promoted from a pure, already formed TiN target with special precautions against contamination;

(ii) the reactive sputtering starting from titanium and nitrogen, usually requires two or several subsequent steps, i.e. vaporization and deposition followed by a thermal annealing treatment.

Sputtered TiN films are commonly formed by reactive *in situ* sputtering (RIS) of titanium in nitrogen/argon ambient, or by thermal conversion of titanium in nitrogen or NH_3 ambient.

We note, however, that the ion bombardment in most cases degrades the properties due to excess gas trapping. The amount of trapped gas is often larger than can be accommodated in the crystal lattice, resulting in gas bubble formation.

For localized surface protection, as required in electronic or micromechanical applications, it is advantageous to use a deposition technique that can lead to the desired small-size deposit in a single step.

Lasers also have been applied for the synthesis and/or the deposition of thin layers of TiN. LCVD starting from precursors such as $TiCl_4$, nitrogen and hydrogen has proved succesful in obtaining quality deposits of stoichiometric TiN [13–17]. We note, however, that for larger incident laser powers the profile of the films obtained by LCVD begin to show the doubled-humped "volcano" shape [18]. We obtained the surface nitridation of titanium targets by multipulse excimer laser irradiations in a slightly superatmospheric ambient nitrogen at a level of the incident laser fluence of $0.6–1.4\ \mathrm{J\,cm^{-2}}$ (τFWHM ≥ 30 ns) [19–22]. The nitride layer growth was precisely within the location of interest. For obvious reasons, the thickness of this layer is limited due to the limitation of the gas access towards the inner, unreacted titanium.

We propose an approach aimed at both the synthesis and deposition of high quality TiN films in

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a one-step procedure [23, 24]. For this purpose we used multipulse excimer laser ablation of a titanium target in a low pressure (a few tens of micro bars) of nitrogen. The incident laser fluence was increased to 4–5 J cm^{-2}, while the forming compound was collected on a silicon support placed parallel to the titanium target at a distance of 8–15 mm. This process has been called laser-reactive ablation (LRA).

In order to evaluate the actual potential as well as the limits of LRA in obtaining good quality thin films we continued our investigations with a parametric study in relation to the total pressure of the ambient gas.

2. Experimental procedure

High-purity (99.6%) titanium targets with dimensions of $10 \times 10 \times 3$ mm^3 were used. Irradiation was conducted with an excimer laser source (Lambda Physics model LPX 315 i). The laser source was operated with XeCl* as an active mixture ($\lambda = 308$ nm) delivering pulses of $E_0 = 0.2$–0.3 J energy and τFWHM $\sim$ 30 ns duration at a repetition rate of $f = 10$ Hz. The laser radiation was focused in order to obtain a typical incident laser fluence of 5 J cm^{-2}. The laser beam was incident at an angle of about 45° on the surface of the titanium target on locations eccentric slightly with reference to the geometrical centre of the target. In order to obtain irradiation conditions as uniform as possible, the target was rotated during the application of the multipulse laser treatment with a 3 Hz rotation frequency.

All irradiation was conducted inside a stainless steel high-vacuum chamber. The chamber was first evacuated down to 10^{-6} mbar, while its walls were heated in order to facilitate the desorption of water vapour. Then, a jet of very pure nitrogen (electronic grade 99.999%, with less than 2 p.p.m. oxygen) was continuously blown inside the chamber which was accurately set at a chosen value in the 1 μbar–10 mbar range.

The material ablated under laser irradiation was collected on a silicon wafer which was positioned parallel to the titanium target at a separation distance of $d = 15$ mm. The collectors were produced from very pure (1 0 0) single-crystalline silicon wafers. Before introduction into the irradiation chamber, every collector was carefully cleaned with alcohol and then with a solution of 10% HF in de-ionized water. In this way, an efficient removal of the native SiO_2 film is ensured.

The laser irradiation was prolonged in a series of 10 000 pulses.

After completion of an irradiation series, both the target and the collecting support were allowed to cool inside the chamber, in vacuum.

Systematic electron microscopy studies were performed with a Jeol TEMSCAN 200 CX installation in either a scanning electron microscope (SEM), transmission electron microscope (TEM), or selected-area electron diffraction (SAED) modes.

The X-ray photoelectron spectroscopy (XPS) studies of the deposited film were conducted with the aid of an ESCALAB MK II apparatus. An unmonochromatized X-ray source was used with an aluminium anode (1456.6 eV). The spectra calibration was achieved as against the Ag 3d5/2 (368.26 eV) and Ag *M4NN* (1128.78 eV) lines with the Fermi level as a reference level. The correction of the charging effects was obtained with a flood gun by following the position of the C 1s line (285 eV). We studied the Ti 2p doublet.

The vacuum enclosure of the instrument was first evacuated down to a pressure of 10^{-9} mbar.

The microhardness of the obtained films was measured with a PMT 3 apparatus, and the sheet resistivity–conductivity of the films containing TiN was determined with a JANDEL four-probe instrument.

3. Results

3.1. Visual inspection

The layers deposited in a rather wide range of nitrogen pressure exhibit a yellowish colour, characteristic of TiN coating. The yellow colour is the most intense for a pressure, p_0, up to several tens of microbars, when the colour turns to yellow-blue, becoming largely light blue with white touches at a pressure of 1 mbar.

3.2. Electron microscopy investigations

We have investigated the films obtained over the whole range of pressures of ambient nitrogen. The main results of these studies are collected in Table I. A first observation emerging from the inspection of the data collected in Table I concerns the existence of a rather wide pressure range between 7 and 70 μbar for which the laser-reactive ablation (LRA) makes it possible to obtain quite pure, rather well-crystallized layers of f c c TiN. The layers are uniform with crystallites of 10–15 nm (Figs 3a and 4a). The film thickness changes very slowly with the ambient pressure value and is of the order of 200–500 nm (see, for example Fig. 5a).

For a lower ambient pressure (Figs 1 and 2) of a few microbars, the deposited TiN is amorphous and mixed with amorphous silicon. The weak reflections

TABLE I The main features of the films deposited by LRA of TiN in nitrogen at a variable pressure, p_0, resulting from electron microscopy (TEM, SAED) studies

Pressure (μbar)	Description of the deposited film	Fig.
0.6	Traces only of amorphous TiN embedded in amorphous silicon	1
2	Mixture of amorphous TiN and amorphous silicon	2
7	Polycrystalline f.c c TiN with crystallites of 10–15 nm	3
13		
33		4
70		5
130	Oxidized polycrystalline TiN most probably oxynitride of the type (TiN_xO_{1-x}) with crystallites of 5–10 nm	6
330	Mixture of amorphized TiN and amorphized TiO	7
10 000	Poorly crystallized TiO_2 with crystallites of a few nm	8

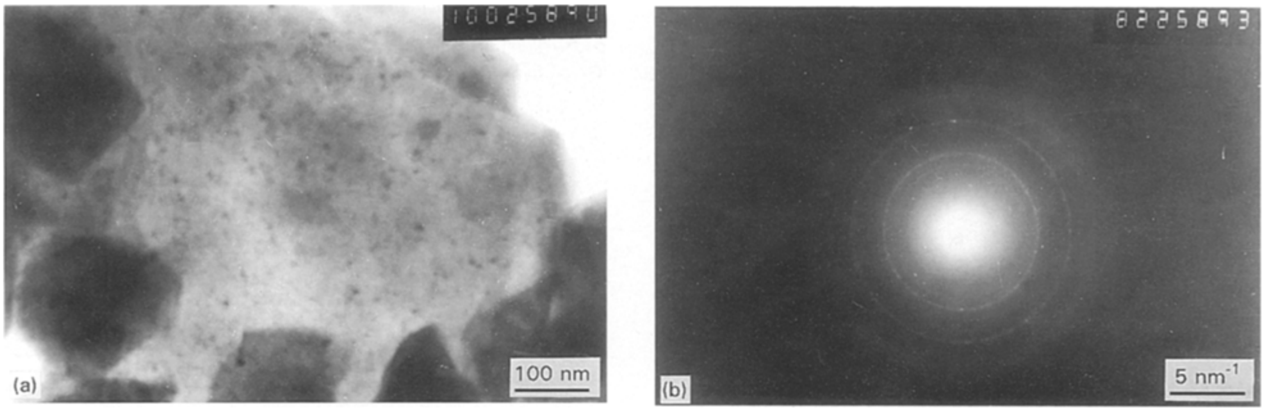

Figure 1 (a) A typical transmission electron micrograph and (b) the corresponding SAED pattern recorded for a film obtained at a pressure $p_0 = 0.6$ μbar of ambient nitrogen.

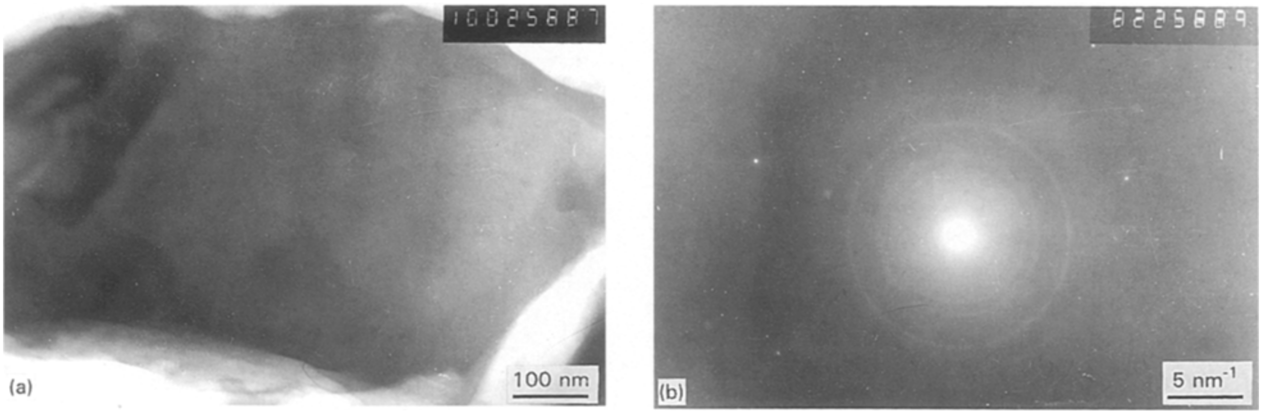

Figure 2 (a) A typical transmission electron micrograph and (b) the corresponding SAED pattern recorded for a film obtained at a pressure $p_0 = 2$ μbar of ambient nitrogen.

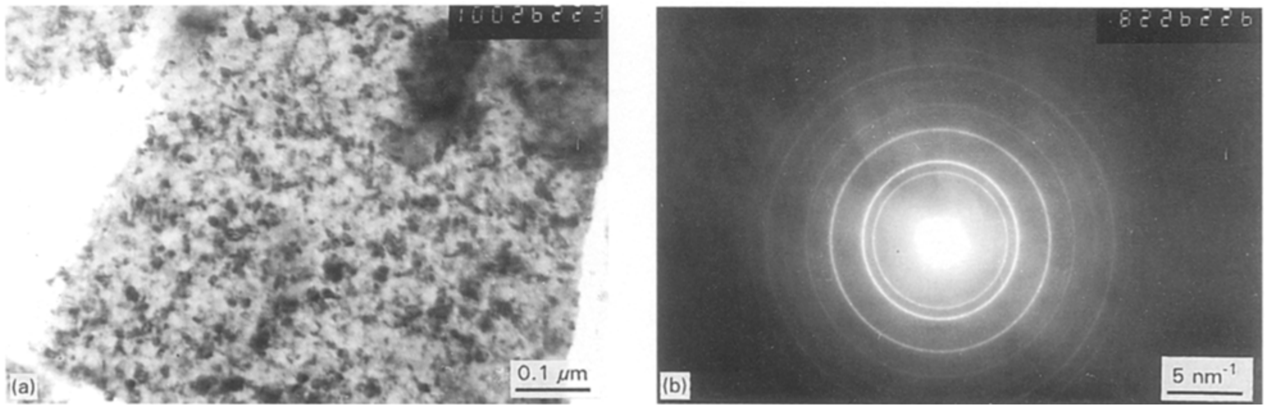

Figure 3 (a) A typical transmission electron micrograph and (b) the corresponding SAED pattern recorded in the case of a film obtained at a pressure $p_0 = 7$ μbar of ambient nitrogen.

belonging to TiN come from very small crystallites that are practically embedded in the prevalent amorphous silicon.

A quite unexpected behaviour was observed when increasing the nitrogen pressure in excess of 100 μbar (Figs 6–8). The presence of TiN in the deposited films gradually vanishes. The oxide content becomes more and more important when p_0 increases to 130 μbar (Fig. 6) and especially to 330 μbar (Fig. 7). For a gas pressure of a few millibars (Fig. 8), only TiO_2 is deposited and the films are much thinner. Whenever the extraction replica included slices originating from the single-crystalline silicon substrate, we could perform a more elaborate, quantitative analysis, of the SAED patterns. We inferred that the lattice parameter is $a_0 = (0.423 \pm 0.001)$ nm in the case of the films obtained at $p_0 = 7$ μbar (Fig. 4b). The lattice parameter is rather different, $a_0 = (0.420 \pm 0.001)$ nm at $p_0 = 130$ μbar (Fig. 7b).

We note that according to ASTM 6-0642 [25], the lattice constant of pure TiN has a value $a_0 = 0.424$ nm, while the lattice constant of TiO_2 (NaCl-structure phase) is $a_0 = 0.414$ nm. Consequently, we can conclude that the film deposited at

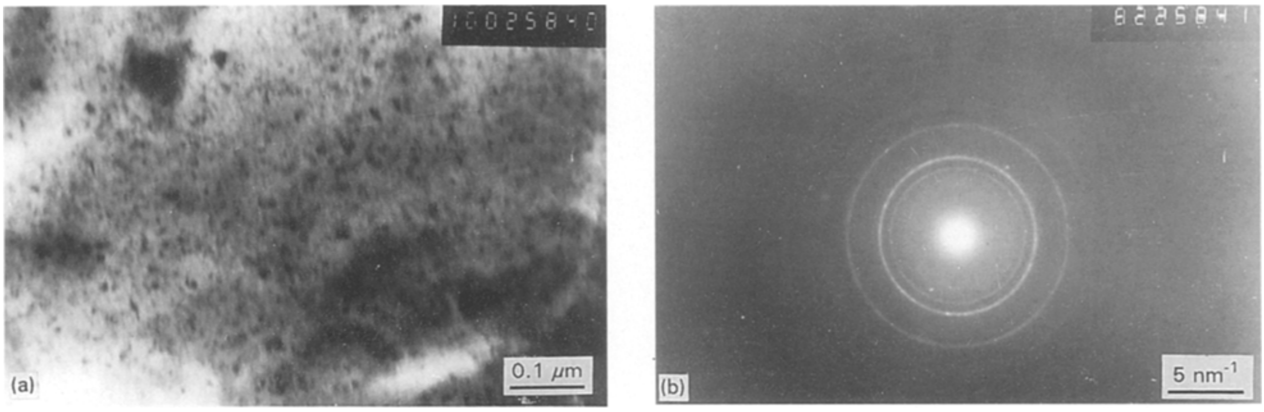

Figure 4 (a) A typical transmission electron micrograph and (b) the corresponding SAED pattern recorded for a film obtained at a pressure $p_0 = 33$ μbar of ambient nitrogen.

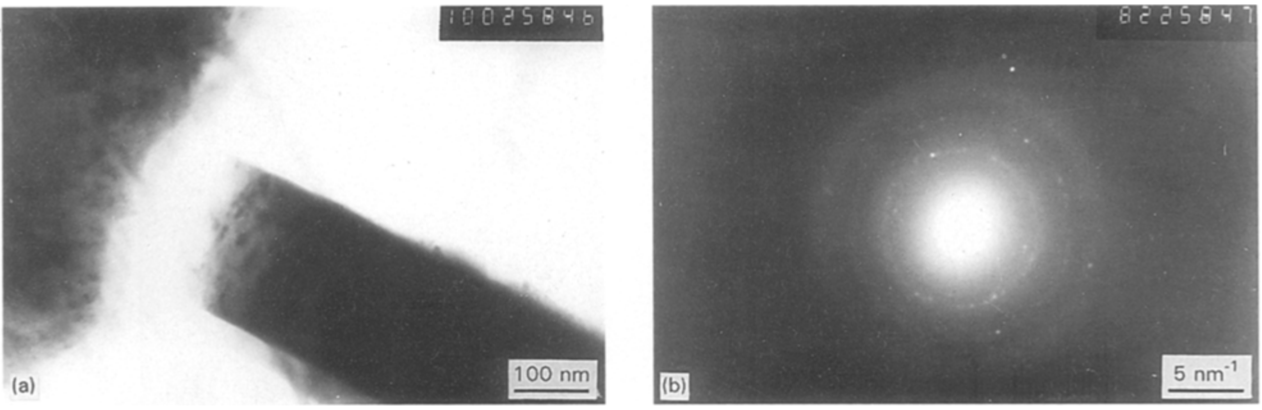

Figure 5 (a) A typical transmission electron micrograph and (b) the corresponding SAED pattern recorded in the case of a film obtained at a pressure $p_0 = 70$ μbar of ambient nitrogen; we succeeded in recording the forming film in cross-section from which we can deduce a film thickness of ~210 nm.

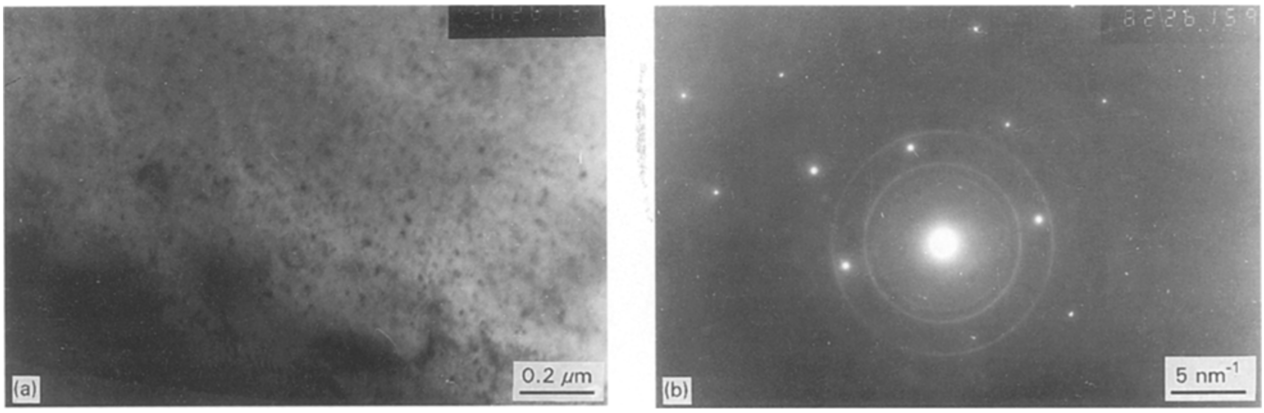

Figure 6 (a) A typical transmission electron micrograph and (b) the corresponding SAED pattern recorded for a film obtained at a pressure $p_0 = 130$ μbar of ambient nitrogen.

$p_0 = 7$ μbar is, in fact, fcc TiN, while for $p_0 > 100$ μbar, the crystalline lattice of TiN gradually accommodates oxygen resulting in the formation of an oxynitride compound of the type TiN_xO_{1-x} [26].

Accordingly, the lattice constant falls to $a_0 = (0.420 \pm 0.001)$ nm approaching the value characteristic of the TiO_2 oxide.

When further increasing the pressure, P_0 to several hundreds of microbars, reflections belonging to TiO_2 become clearly visible (Figs 7b and 8b). Finally, at several millibars (Fig. 8b) only the reflections of TiO_2 are evident.

3.3. Electron spectroscopy investigations

According to Sundgren *et al.* [27], the 2p line of the titanium peaks, in the case of unbound titanium, at 454 eV. The normal position of this line corresponding to the Ti–N bond (in TiN) and the Ti–O bond (in TiO_2), respectively, are marked in Fig. 9. The recorded spectra reveal the presence of TiN for a pressure of ambient nitrogen in the range of 7–70 μbar (Fig. 9) [28]. In addition to the TiN phase, one notices in Fig. 9 the significant presence of the Ti–O bond in the form of the TiO_2 phase. We note that the presence of oxide is, in fact, expected because the XPS collects

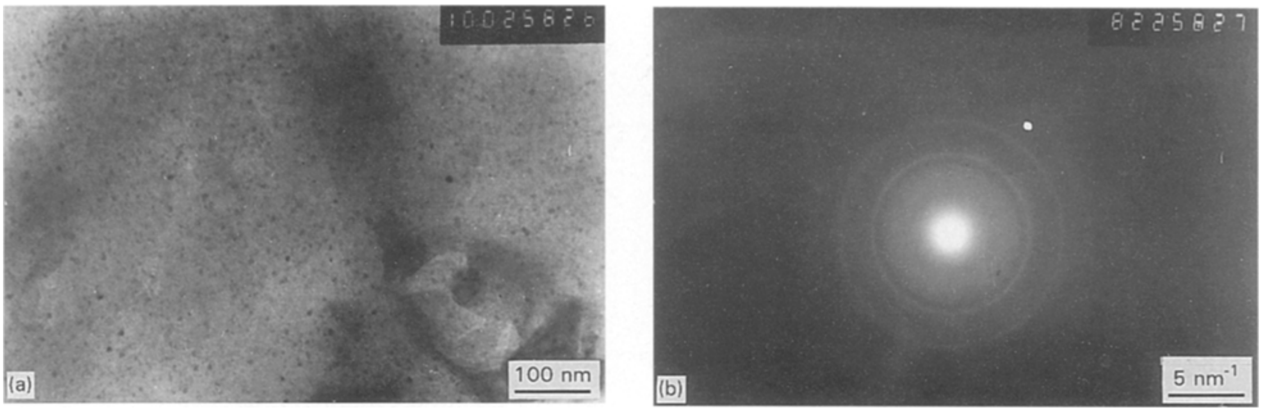

Figure 7 (a) A typical transmission electron micrograph and (b) the corresponding SAED pattern recorded in the case of a film obtained at a pressure $p_0 = 330\ \mu$bar of ambient nitrogen.

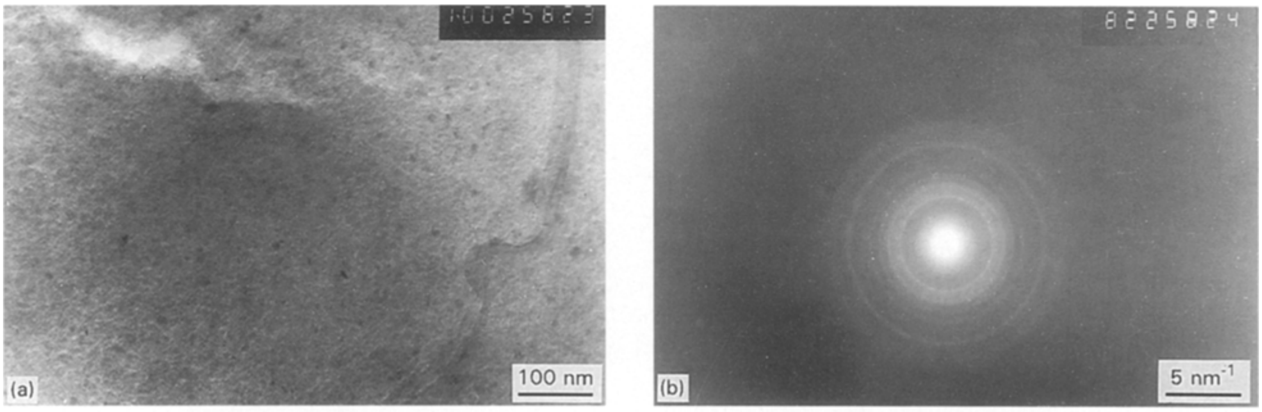

Figure 8 (a) A typical transmission electron micrograph and (b) the corresponding SAED pattern recorded for a film obtained at a pressure $p_0 = 10$ mbar of ambient nitrogen.

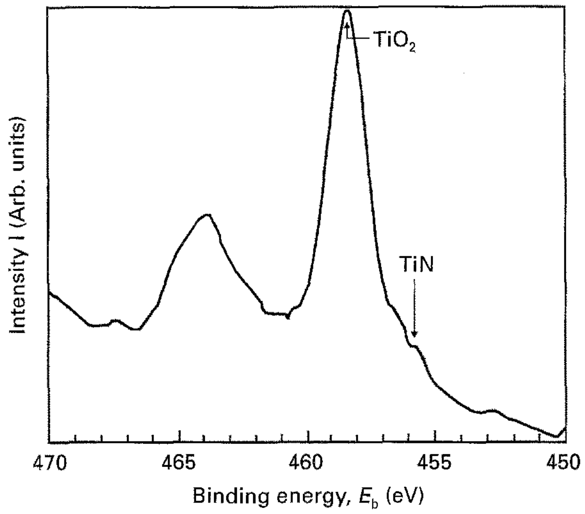

Figure 9 A typical XPS spectrum corresponding to the film obtained at $p_0 = 33\ \mu$bar.

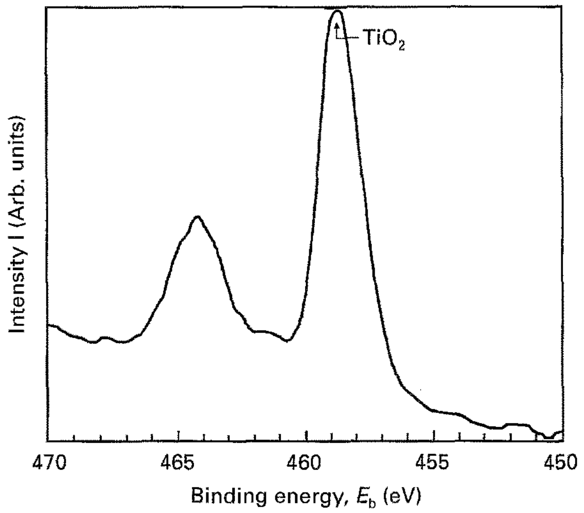

Figure 10 A typical XPS spectrum corresponding to the film obtained at $p_0 = 5$ mbar.

information from the top film of the deposited layer with a thickness of 2–6 nm only, which is always contaminated with oxygen due to contact with air [29, 30]. We emphasize the fact that the relative weights of the two peaks indicating the existence of the Ti–N and Ti–O chemical bonds, remain unchanged when scanning the surface of a certain film obtained in the 7 μbar $\leq p_0 \leq$ 70 μbar pressure range. Most of the samples contain only TiO_2 (Figs 9 and 10). This is particularly true for the films deposited at a pressure of ambient nitrogen larger than 300 μbar (Fig. 10).

3.4. Microhardness determinations

As expected, the presence of TiN in the deposited layers results in an overall increase in surface microhardness as compared to the rather high background value, characteristic of the uncounted silicon (of

6 GPa). We recorded experimentally values of 10–11 GPa in the case of layers obtained for p_0 within the range 2–130 μbar. An abrupt fall in microhardness in the films deposited at $p_0 \sim 1$ mbar to a value of 8 GPa is seen.

3.5. Four-probe determinations

The deposition on to the silicon collector of a layer containing titanium nitride was confirmed by four-probe measurements which showed rather large conductivity values as being characteristic of this "metallic-like" compound. We measured a conductivity value of $\sim 2\text{–}5 \times 10^4\ \Omega^{-1}\ \text{cm}^{-1}$ in the case of films obtained at $p_0 = 2\text{–}130$ μbar. We note that the conductivity values determined by us in the case of films containing titanium nitride are in good agreement with the handbook data [31]. As expected, the handbook data, which are, in fact, bulk determinations corresponding to solid massive samples of standard TiN, are slightly larger. In any case, the introduced values of the electrical conductivity characteristic of the films deposited by LRA of titanium in nitrogen in the optimum pressure range are larger than the characteristic values for pure titanium [32] $(1\text{–}3) \times 10^4\ \Omega^{-1}\ \text{cm}^{-1}$ and much larger than the conductivity on the silicon collector substrate.

On the other hand, the conductivity of the layers obtained decreases by one order of magnitude when the nitrogen pressure is further increased to several hundreds of microbars. Finally, no determinations were possible in the case of layers obtained at p_0 of a few millibars.

4. Discussion

The most remarkable piece of evidence reported in the previous section of this paper is the existence of a rather extended pressure range for which LRA of titanium in nitrogen results in the deposition of good-quality f c c TiN films without a detectable contamination with oxides. Indeed, for a pressure 7 μbar $\leq p_0 \leq$ 70 μbar, there are enough nitrogen atoms to nitridate all of the expelled titanium atoms, while the oxygen impurities in gas do not interfere in the chemical reaction. The films obtained in this pressure range have only a very superficial contamination with oxides. The oxygen contamination is visible only in the XPS spectra, and were not evident in electron diffraction of the extraction replicas which integrates information from the entire deposited layers.

As showed in detail in Section 3.2, at $p_0 > 100$ μbar the oxygen traces in the reaction gas begin to interfere. In the beginning, the TiN molecule accommodates some oxygen. An oxynitride compound of the $\text{TiN}_x\text{O}_{1-x}$, type is formed. Then together with the increase in p_0 up to 1 mbar and above, titanium oxides only are deposited on the silicon collector. We observe that the exposure to oxygen between two subsequent laser pulses is:

$$\text{EO}_2 = 2 \times 10^{-6}\, p_0(\text{torr})/f(\text{Hz}) \qquad (1)$$

For $p_0 = 130$ μbar (i.e. the first ambient pressure value for which the deposition of the oxynitride compound is observed), we obtain from Equation 1 an exposure to oxygen of only 0.02 L. On the other hand, corresponding to a deposition rate of 0.2–0.5 nm/pulse, a fraction that is the equivalent of one-tenth of a molecular layer is deposited after the action of a single laser pulse. This means that while the deposition of a layer is completed, the substance undergoing laser ablation is, in fact, in contact with an exposure to oxygen ten times larger, i.e. of 0.2 L.

Owing to the extreme chemical activity of titanium when in contact with oxygen, this presence of oxygen is instantaneously materialized in its inclusion by the forming chemical compound that accommodates approximately 20% oxygen. Consequently, at this pressure an oxidized titanium nitride is deposited of the $\text{TiN}_x\text{O}_{1-x}$ type where, most probably, $x \geq 0.8$ and $1 - x \leq 0.2$.

The titanium oxynitride becomes unstable when it accommodates too much oxygen [26]. This happens at $p_0 = 330$ μbar when, according to Equation 1, x is reduced to 0.5 and below. The oxynitride molecule is broken [26] and the clear presence of TiO_2 (brookite) is evident.

For larger values of p_0 of the order of a few bars, the exposure to oxygen becomes larger than 1 L. The process is dominated by the participation of oxygen in the chemical reaction and only titanium oxides are deposited. Another deposition regime was observed at lower pressures of the ambient nitrogen of several microbars. Then a deficit of nitrogen occurs. In addition, the titanium particles expelled by laser ablation are more energetic at the moment of their impact on to the collector. The titanium "projectiles" cause the dislocation of a certain quantity of silicon atoms from the single crystalline substrate. As an effect, the deposited film is, in fact, a mixture of amorphous TiN with amorphous silicon and traces of unbound (unreacted) titanium.

5. Conclusion

We have demonstrated that the application of LRA to the deposition of TiN layers exhibits a clear optimum behaviour in relation to the value of gas pressure.

Pure f c c TiN films are obtained for a pressure larger than 7 μbar but not in excess of 70 μbar. The further increase of p_0 is accompanied by a strong activation of the oxygen impurities in the reaction gas. This is made evident by the deposition of films with an important and finally prevalent contamination. The lower the oxygen impurity of the gas, the larger is the pressure range in which pure f c c TiN films are synthesized and deposited. Conversely, using gases with a larger contamination of oxygen, the optimum pressure range is strongly narrowed, to the point of its complete elimination.

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