

Bias-induced stress transitions in sputtered TiN films

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We report on intrinsic stress properties of magnetron sputtered titanium nitride films deposited under different conditions. By proper selection of processing parameters, films with low stress can be obtained. Unstressed film formation is favored by low substrate bias voltage, high pressure, or use of heavy sputtering gases. Stress relief is, however, accompanied by an increase in resistivity and a decrease in film density. As a result of these changes the effectiveness of such titanium nitride films as diffusion barriers between silicon and aluminum is minimal.

I. INTRODUCTION

Titanium nitride (TiN) is among the most promising diffusion barrier materials for semiconductor contact metallizations. Its effectiveness in this application is believed to lie on its thermodynamic stability.¹ Properties of TiN in thin film form are, however, strongly dependent on the selected deposition method and its process parameters. When sputtering is employed in which the growing film is continuously under exposure to energetic particle bombardment (ions, neutral atoms), compressive stress is commonly created.^{2,3} High stress, either in as-deposited films or when thermal stress is superimposed on intrinsic stress during heat treatments, causes mechanical problems, such as total peeling off or localized blistering.⁴

Most of the reported investigations of stress in sputtered films have exploited elemental metals.⁵ Abrupt transitions from tensile or unstressed to compressive state take place as a function of various deposition parameters, such as pressure, substrate or target voltage, or the angle of the incident flux relative to the substrate surface. The origin of the compression is believed to be recoil implantation of the film elements or working gas entrapment, both being caused by energetic particle bombardment of the film surface.⁵ Under conditions favoring large energy of bombardment (low pressure, high voltage, light working gas with respect to the mass of the target, etc.), strongly stressed films of low electrical resistivity and high optical reflectivity are formed. The film transforms from an open columnar to a dense fibrous state when surpassing such threshold of growth conditions,⁶ which results in the observed simultaneous transitions of stress, resistivity, and reflectivity.

Stress properties of sputtered titanium nitride films have been measured and are often reported to be somewhat higher than those of simple metals: 1–10 GPa ($1-10 \times 10^{10}$ dyn/cm²).⁷⁻¹⁰

The purpose of this work was to investigate whether the strong compression of sputtered TiN films can be avoided, and how this stress relief would affect the performance of TiN as a diffusion barrier layer. The substrate bias voltage and the mass of the inert sputtering gas component (Ar, Kr, Xe) were used as process variables. The total pressure was not varied, except in one single experiment, because of the complex relation between the total and partial pressures and the stoichiometry of the resulting film.

II. EXPERIMENTAL PROCEDURES

Thin cover glass slides ($18 \times 18 \times 0.175$ mm³) were used as substrates. Before depositions they passed through organic cleaning steps in ultrasonic baths of TCE, acetone, and methanol.

Titanium nitride films of thicknesses varying between 65–140 nm were then deposited by reactive rf sputtering from a Ti target placed in contact with a planar magnetron cathode (75 mm in diameter). An additional dc voltage source was used for biasing the substrate table whose dimensions were large compared to the target. The distance between the target and the substrate table was approximately 7 cm. The system was equipped with an oil diffusion pump and a chiller trap, capable of evacuating the sputtering chamber to a base pressure of approximately 6×10^{-5} Pa (4.5×10^{-7} Torr). Throttling the pumping port for the sputtering process increased the base pressure by a factor of 4. The total sputtering pressure of 1.33 Pa (10 mTorr) of premixed gas compositions of 80% Ar/20% N₂, 80% Kr/20% N₂, or 75% Xe/25% N₂ (in relative partial pressures) was adjusted with a variable leak valve, and monitored with a capacitive manometer. A larger proportion of nitrogen was needed with Xe (25%) than with Ar or Kr (20%) to maintain the stoichiometry of the deposited TiN films (TiN_x, $x \approx 1$). Total pressure of 1.87 Pa (14 mTorr) was used in one case by increasing the Kr partial pressure in the Kr/N₂ mixture while keeping the N₂ partial pressure constant.

The target surface was conditioned by presputtering for 2 min with a rf power of 800 W and with the final gas composition by keeping the target shutter closed. Five substrates were then exposed to the glow discharge one after each other, so that the applied dc substrate bias was adjusted between depositions from -20 to -100 V. Deposition rates with the applied rf power of 800 W were in all cases 40 nm/min ($\pm 5\%$). The fact that this rate was only one third of that achieved upon sputtering in low nitrogen partial pressures or in pure argon indicates that the target surface was covered with a nitride layer during the depositions described here.

One comment is appropriate at this point. When interpreting the results of our experiments, one observes that it is, indeed, the energy flux due to the bombarding particles of the discharge that controls the structural properties of the growing film. Mass or energy analysis of this flux have not been performed in the course of these experiments. Only

rough estimates of the upper limits of the energies involved are possible. The dc bias is able to generate singly ionized species of up to 100 eV onto a conductive substrate. In our case for insulating glass substrates the effective bias is evidently less than that. Another source of energetic species is the cathode sheath. The average electrical potential of the cathode was measured to be -750 , -820 , and -880 V for Ar/N₂, Kr/N₂, and Xe/N₂ sputtering, respectively. Singly ionized species up to around 880 eV can thus be produced. A fraction of these ions is neutralized and reflected toward the substrates. The energy of the reflected particle depends on the mass ratio of the target and the gas atom or molecule involved in the collision.⁵ In our case, a nitrogen atom reflecting from titanium can reach about 260 eV, when calculated as in Ref. 5, while other collision processes yield lower values than that. However, there is also evidence in the literature that when light targets are bombarded by heavy ions, the energy of the neutrals bombarding the substrates is larger than that obtained from this simple calculation.¹¹ The total energy flux onto the substrates is thus difficult to estimate, and it depends on the configuration of the sputtering apparatus used, the nature of the target and substrate bias, the gas composition and pressure, as well as the ionization in the discharge affected by the applied magnetic field.

The film stress was determined by measuring the resulting deflection of the samples. A stylus instrument (Sloan Dektak) was used to acquire cross-sectional profiles of deflection from which the quadratic coefficients k were calculated assuming parabolic profiles. The average incremental film stress was then derived with the commonly applied formula⁵

$$\sigma_{av} = \frac{E_s t_s^2 k}{3(1 - \nu_s) t_f},$$

where E_s , t_s , and ν_s are the elastic modulus, the thickness, and the Poisson ratio of the substrate, respectively ($E_s = 50$ GPa, $\nu_s = 0.22$ for soda lime glass^{5,12}), and t_f is the thickness of the film. The derived intrinsic stress values have some uncertainty because of the facts that film thicknesses were calculated from ion backscattering spectra assuming N:Ti ratio of 1:1 and bulk density of TiN for all films (5.22 g/cm³),¹³ the thermal component of the stress was neglected (in fact, thermal expansion coefficients of soda lime glass¹⁴ and TiN¹⁵ are both about 9×10^{-6} /K), and the average incremental stress was assumed to be constant during deposition. In addition, samples with small deflections (low stress) may have a contribution by the original deflections of the glass substrates, which were not taken into account.

Film resistivities were determined from four-point probe measurements and from film thicknesses derived from 2 MeV ⁴He⁺ backscattering (BS) spectra. Densities of some films were determined in the following fashion. The amount of Ti atoms/cm² was calculated from BS spectra. The stoichiometry (x of TiN _{x}) was obtained with the nuclear resonance broadening method (NRB) using the $E_p = 429$ keV resonance in the reaction ¹⁵N($p, \alpha\gamma$)¹²C and comparing the γ -ray yield with that measured from pure TiN powder standard,¹⁶ resulting in the amount of N atoms/cm². The concentrations of impurities like O, Ar, Kr, or Xe were obtained

from BS spectra on glass or C substrates, but they did not have a significant contribution to film density. After photolithographic patterning in an EDTA solution,¹⁷ the physical thicknesses of the films were measured with the stylus instrument. These data are sufficient for density derivations.

The stability of two different TiN films (~ 40 nm thick) as diffusion barriers between single crystalline Si and sputtered Al (~ 400 nm thick) was measured. The TiN and Al films were sequentially deposited without breaking the vacuum. The samples were annealed in vacuum ($\sim 10^{-4}$ Pa) at 500 °C for 30 min, and the resulting interdiffusion was analyzed by BS.

III. RESULTS

The intrinsic stress of all our sputter-deposited TiN films is compressive with values varying up to 9 GPa (9×10^{10} dyn/cm²). When low substrate bias voltages are used, films with low stress (< 2 GPa) are obtained, but with increasing bias a rapid transition to high compression (4–9 GPa) takes place at a certain threshold value, see Fig. 1. The transition region in our sputtering system is narrower than 20 V of applied dc bias, and the threshold value depends on the sputtering parameters, like for example the mass of the inert gas. The heavier the gas atoms are, the higher is the threshold voltage. The effect of the chamber pressure to the threshold is seen in Fig. 2. The two curves are recorded with 8:2 and 12:2 pressure ratios of Kr:N₂ in the sputtering gas at total pressures of 1.33 and 1.87 Pa, respectively, as a function of the bias voltage. The bias threshold shifts from approximately -50 to -65 V when the pressure is increased.

The electrical resistivities of the samples of Fig. 1 are shown in Fig. 3. The values range from 30×10^{-8} to 100×10^{-8} Ω m, so that films sputtered with high bias exhibit smallest values. Thresholds exist also in the resistivity curves like in the stress curves, although the relative shifts are not quite as large in magnitude. They take place at roughly the same bias values in both cases. This fact can be clearly seen in Fig. 4, in which the data of Figs. 1–3 are reproduced

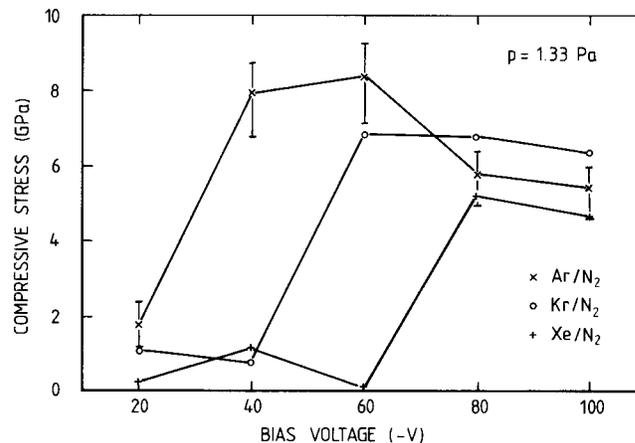


FIG. 1. Intrinsic compressive stresses of Ar/N₂, Kr/N₂, and Xe/N₂ sputtered TiN films on glass substrates as a function of dc substrate bias voltage. The estimated inaccuracy of the stress measurement is shown for the case of Ar/N₂ sputtering only.

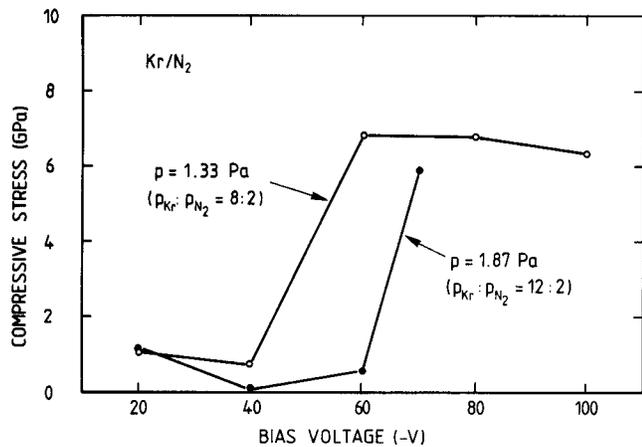


FIG. 2. Intrinsic compressive stresses of Kr/N₂ sputtered TiN films on glass substrates as a function of dc substrate bias voltage. The curves represent samples sputtered at different Kr partial pressures.

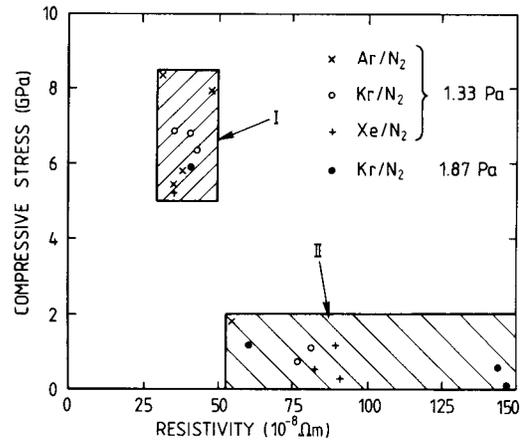


FIG. 4. Electrical resistivities of samples of Figs. 1 and 2 as a function of their intrinsic compressive stress. Note that films exhibit either high stress and low resistivity (group I) or low stress and high resistivity (group II).

in a form of a stress versus resistivity plot. The existence of two separate groups of samples is observed. This separation has been confirmed by measuring properties of several additional TiN films from glass, Si, and Si/SiO₂ substrates, showing values within the shaded areas of Fig. 4. Group I films have high stress (4–9 GPa) and low resistivity (30–50 × 10⁻⁸ Ω m), and group II films have low stress (0–2 GPa) and high resistivity (> 50 × 10⁻⁸ Ω m).

Further film characterization was done assuming that the rough division into group I and group II samples, shown in Fig. 4, is generally valid. One or a few samples were picked from each group and their stoichiometry, density, oxygen and inert gas concentration, and diffusion barrier properties were measured and compared.

The NRB method was used to determine the N/Ti atomic ratio *x* of four samples, two of them from group I (Ar-100 V, Kr-100 V) and two from group II (Kr-40 V, Xe-40 V), see Fig. 5. All films have excess nitrogen with the exception that Kr-100 V seems to have a transition during growth from nitrogen deficiency to excess. The lowest and the highest average *x* values belong to group I samples and the two intermediate curves are from group II samples. Thus, in this respect no difference is observed between the two types of

films, and an average film composition TiN_{*x*}, *x* = 1.1 ± 0.05, is recorded for all samples at least in the bulk of the film.

BS measurements of TiN films on glass, Si, and C substrates did not give much information about the impurities involved, because the levels are close to the detection limits of the technique. The concentrations of oxygen and the inert sputtering gas component show a smooth change with the bias voltage rather than any sharp transitions. The Xe or Kr contents of the films increase from less than 0.1 to about 0.3 at. % when substrate bias is increased from -20 to -100 V. The corresponding Ar contents are of the same order of magnitude, but too low to be accurately determined by BS. Oxygen concentrations could be measured from films sputtered onto C substrates, but a clear separation could not be

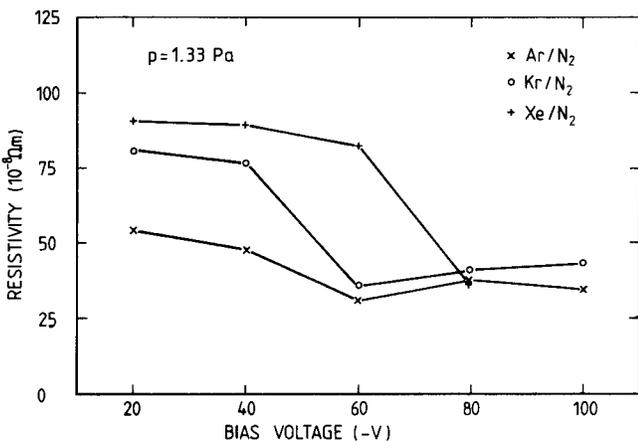


FIG. 3. Electrical resistivities of Ar/N₂, Kr/N₂, and Xe/N₂ sputtered TiN films as a function of dc substrate bias voltage.

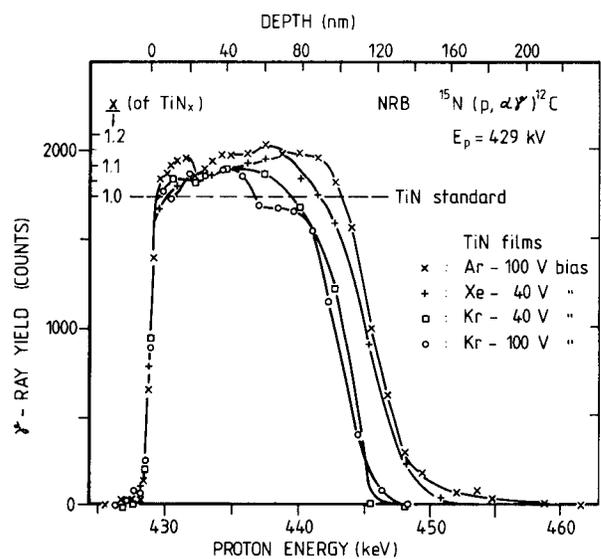


FIG. 5. Concentration profiles of ¹⁵N in bias-sputtered TiN_{*x*} films in comparison to the concentration in standard powder TiN, as measured with the nuclear resonance broadening method (NRB). The proton energy scale of the lower abscissa is converted to the depth scale in the higher abscissa. The films have excess nitrogen close to the composition TiN_{1.1}.

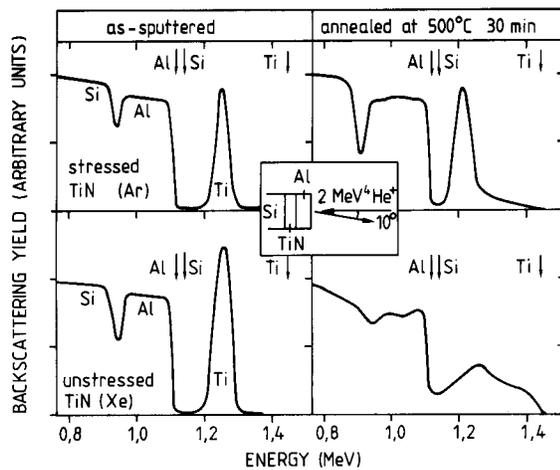


FIG. 6. BS spectra of two different Si/TiN (~ 40 nm)/Al (~ 400 nm) samples before and after annealing at 500°C for 30 min. The upper figures correspond to samples with highly stressed TiN film and the lower figures to samples with unstressed TiN film. The latter is inferior to the former in thermal stability.

made between group I and group II samples. With increasing bias, (-20 to -80 V) a decrease in oxygen concentration from about 4.6 to 3 at. % was measured.

Densities calculated from Dektak, BS, and NRB measurements are 4.32 g/cm^3 for the unstressed film (Kr-40 V) and 4.74 g/cm^3 for the stressed film (Kr-100 V) corresponding to 83% and 91% of the bulk density of TiN (5.22 g/cm^3).¹³

Diffusion barrier properties of an unstressed Xe-sputtered TiN film and a stressed Ar-sputtered TiN film (-60 V bias) between Si substrates and Al overlayers were investigated by annealing the samples in vacuum at 500°C for 30 min. Figure 6 shows the respective BS spectra indicating that none of the two barriers is perfectly stable in this treatment. Titanium from the stressed film interacts somewhat with the Al overlayer (top figures) while the unstressed TiN is not barrier at all but participates in large scale interdiffusion and reactions (bottom figures).

The principal results for TiN films sputtered using high and low negative substrate bias voltage are summarized in Table I.

IV. DISCUSSION

Very similar studies to these have been performed simultaneously elsewhere.⁷ The goal in both cases has been to develop a process for the deposition of high performance

TABLE I. Properties of sputtered TiN films deposited using high and low substrate bias voltage.

Bias	High	Low
Resistivity ($\Omega\text{ m}$)	$30\text{--}50 \times 10^{-8}$	$> 50 \times 10^{-8}$
Stress (GPa)	4–9	0–2
N/Ti	1.1	1.1
O (at. %)	3	4.6
Kr, Xe (at. %)	~ 0.3	< 0.1
Density (g/cm^3)	4.74	4.32
Al barrier	good	bad
Color	goldish	brownish

TiN diffusion barriers incorporating low stress. The approach to the problem has also been quite similar, but the results are drastically different: in Ref. 7 unstressed “TiN” (in fact $\text{Ti}_{26}\text{N}_{39}\text{O}_{21}\text{C}_{13}$) forms a stable diffusion barrier in a Si/Ti/TiN/Pt/Au metallization system, but in our work the unstressed Si/TiN/Al structure is highly unstable.

From Figs. 1 and 2 one concludes that the intrinsic stress of TiN films can be affected by various process parameters. When a parameter is changed in such a way that the energy of the particle bombardment of the film surface is increased, stressed film formation is favored. (i) The increasing bias voltage increases the energy of the ions accelerated by the sheath field. (ii) Decreasing the atomic mass of the sputtering gas with respect to that of the target increases the energy of the neutrals reflecting from the target surface and traversing to the substrates.¹¹ (iii) Decreasing the total pressure lessens the energy loss of the particles by collisions. All these parameters participate in determining the total energy of bombardment, but in a smoothly varying fashion. The film properties, instead, exhibit an abrupt transition between two states, so that films with intermediate properties are rare. The same effect has been reported for TiN⁷ and for several other materials.⁵ Thus the concept of a threshold energy seems reasonable. Above that, the film structure is controlled by different atomic processes than below, e.g., by forward sputtering, implantation of the film elements or inert gas into the film, or bombardment enhanced surface diffusion.¹⁸

Figures 3 and 4 show that the electrical resistivity changes together with the stress. Visual inspection of the samples also reveals slight differences in film color: group I films are golden yellow, but group II films generally have a brownish tone. The optical differences may result either from varying microroughness or from shifts in plasma oscillation wavelength of the free electrons in TiN. Similar changes in film properties to those just described are reported elsewhere,^{7,18,19} too, and are attributed to a structural transition. The fairly large isolated columnar crystallites of the unstressed films are replaced by small grains with expanded interplanar spacing of the stressed films, while the fcc lattice is preserved.⁷ In Ref. 18 a decrease in the lattice parameter is reported with increasing bias, instead.

The compositions of our films are well described by a formula $\text{TiN}_{1.1}$. Impurity contents of ≤ 5 at. % are measured, being mainly composed of oxygen atoms. Not even films sputtered onto grounded substrates show large oxygen concentrations or high resistivities. The reason for this deviation from some literature data^{18,19} for TiN films sputtered without applied bias may be that higher deposition rates (power densities), lower sputtering pressures, or cleaner vacuum conditions are used here than in those experiments.

The density of our unstressed $\text{TiN}_{1.1}$ is approximately 91% of that of the stressed $\text{TiN}_{1.1}$ (70% in Ref. 7), which is again about 91% of the bulk TiN density (close to 100% in Ref. 7). The inaccuracy in the density measurement is fairly large, so that direct comparisons of the absolute values may not be relevant, but the relative differences between the densities of group I and group II films are significant.

The observations reported here are reproducible for

square glass substrates. Corresponding experiments carried out on substrates of other sizes or of different materials gave other results. All substrates displayed a threshold in the stress versus bias voltage curve. For example, the threshold for narrow and long Si beams ($5 \times 30 \text{ mm}^2$) was between 0 and -20 V , and for 2 in. diam Si wafers it was typically more negative than -20 V . It thus appears that the electric field distribution as affected by shape and conductivity of the substrate, is crucial in determining the stress of the deposited film in our dc-biased system.

For the application as thin film diffusion barriers, low atomic diffusivities are needed. One would think that densely packed films are superior in this respect to voided structures. This is, indeed, the case in our work when TiN films are used between silicon substrates and aluminum overlayers. In Ref. 7 the opposite is true for the Ti/TiN/Pt/Au metallization on silicon. In this latter example, however, a fivefold oxygen content is measured from the TiN when compared to our films. This fact supports the suggestion given in Ref. 7 that impurities determine the barrier performance in voided TiN films. A similar effect of impurities has also been observed in vacuum-evaporated TiN/Al metallizations on Si: the TiN barrier that was exposed to air prior to Al deposition was much more stable in heat treatments than the unexposed barrier.²⁰ It is thus possible that the slight interaction of the densely packed stressed TiN film with Al at 500°C (Fig. 6) could be suppressed by impurities. That magnetron-sputtered TiN and Al films deposited sequentially under clean conditions (i.e., in the same vacuum) interact with each other has been observed elsewhere, too.²¹ For dense films the interdiffusion failure is not as fatal as for porous films (Fig. 6).

V. CONCLUSION

When reactively sputtered TiN films are used as diffusion barriers in multilayer metallization systems of semiconductors, the compressive stress of the film is often a problem. There are at least three approaches to a solution. (i) To use as thin TiN layers as possible to minimize the integrated stress. (ii) To use adhesive layers in the critical interfaces. (iii) To sputter the film with low substrate bias, high pressure, or with heavy inert gases to avoid energetic surface bombardment during growth. In this third approach, our results indicate that the reduction of stress also degrades the diffusion barrier properties of the film. A recent independent investigation of stress in reactively sputtered TiN films⁷ comes to conclusions that clearly differ from ours in several important respects. These apparent contradictions vividly demonstrate the rule that the properties of a thin-film diffusion barrier depend critically on just how the film was produced. Thin reactively sputtered TiN films can be good diffusion barriers, but under exactly what deposition

conditions such films can be obtained, and why, remains to be clarified.

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