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Nucleation study of titanium nitride onto steel using $^{15}N(p,\alpha\gamma)^{12}C$ resonant nuclear reaction

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Abstract

In this research, titanium nitride is deposited by reactive DC magnetron sputtering with two original constraints due to the expected industrial application as roll to roll decorative coating of steel: the samples should be grounded and could not be heated during deposition. The growth of titanium nitride on low-carbon steel has been studied using the $^{15}N(p,\alpha\gamma)^{12}C$ resonant nuclear reaction analysis for 429 keV protons. Using gas flow of isotope ^{15}N enriched nitrogen during deposition, it is possible to detect nitride layer of about 0.3 ML (MonoLayer) calculated thickness with the help of the above very sharp nuclear reaction. Films from 0.3 ML to bulk-like thicknesses deposited on low-carbon steel have been analysed. The spectra obtained were deconvoluted to obtain the straggled energy width and the height proportional to the depth of nitride layer and to the ^{15}N coverage, respectively. It is then possible to observe the nitride growth onto steel substrates: an island nucleation is followed by coalescence and finally by a continuous growth. These three nucleation steps suggest an island growth mode, the basis of the well-known columnar structure for sputtered titanium nitride on steel.

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Keywords: Magnetron sputtering; NRA; Titanium nitride; Film growth

1. Introduction

Metal-nitride interfaces play an important role in thin film applications. These two materials have very different physicochemical properties and electronic structures. The understanding of the interfacial phenomenon is of both technological and fundamental interest. In many applications, coverage, bonding and adhesion at the interface are critical for the performances obtained.

The present paper reports the characterisation of titanium nitride growth on low-carbon steel deposited by reactive DC magnetron sputtering without atom mobility induced by either temperature (i.e., the heating) or by intensive ion bombardment (i.e., the sample biasing). These two original constraints are due to the purpose of a more complete study which is the evaluation of the

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DC reactive magnetron sputtering for an expected industrial application as roll to roll decorative coating of low-carbon steel sold as pre-painted coil.

Indeed, the recent developments in reactive sputtering allows high rate coating of large parts [1]. Nowadays, steel strip dry coating plant is then conceivable to replace some industrial polluting wet processes [2]. Pilot plants have already been studied by some authors [3,4]. Previous works have shown that sputtered titanium nitride coating on low-carbon steel can offer a good hardness and a pleasant colour without either biasing or heating during the deposition process [5,6]. Before qualifying TiN_x for industrial application as decorative and protective film, it is important to understand the first stage of the nitride growth on steel and their consequences on the substrate along with coating properties such adhesion or corrosion resistance.

Most of the nucleation studies are conducted with the help of electronic spectroscopy or microscopy [7–9]. But Amsel and Maurel [10,11] have demonstrated that well isolated and strong resonance occurring in nuclear reaction such $^{15}N(p,\alpha\gamma)^{12}C$ at 429 keV can be used to probe near to surface phenomenon. Unfortunately, the relative abundance of ^{15}N in natural nitrogen is only 0.37%. Nevertheless, that reaction offers the possibility of nitrogen depth profiling of sample produced with natural N_2 [5,6] because the peak cross section is more than four orders of magnitude greater than the off-resonance value [12]. If the reactive sputtering is conducted using an Ar and $^{15}N_2$ enriched mixture, very limited quantities of nitride are detected suggesting an alternative way to study the film growth.

2. Experimental procedure

2.1. Samples preparation

TiN_x coatings were produced by DC reactive magnetron sputtering. The vacuum chamber was equipped with a 50 mm diameter magnetron cathode and a 200 l/min turbo molecular pump. The base pressure was less than 5×10^{-4} Pa. The deposition working pressure (argon and nitrogen) and plasma power density were maintained at 0.20 Pa and 11.7 W/cm^2, respectively. The nitrogen partial pressure was fixed at 0.02 Pa during TiN_x deposition. In these conditions, a low temperature (<100°C) yellow-gold film is produced with a nitrogen content of 39 at.% and a cubic face centred lattice (NaCl, $a = 0.424$ nm) at a deposition rate of 0.42 nm/s. If a whole surface coverage is assumed, the deposition rate corresponds approximately to 1 ML/s [5,6].

The low-carbon steel substrates were rinsed in acetone, then plasma etched for approximately 1 min at 0.4 Pa in a pure argon atmosphere prior to nitride deposition. For this growth study, the sputtering was conducted with 98% $^{15}N_2$ enriched reactive gas as discussed above. A precise timer controlled shutter was installed in order to obtain an accurate thickness evaluation. 26 samples had been prepared during deposition times from 0.3 s to several minutes resulting in films with very small calculated thickness (0.1 nm) to bulk-like nitride depth.

2.2. $^{15}N(p,\alpha\gamma)^{12}C$ nuclear reaction analysis

The ^{15}N distribution in the films has been determined using the $^{15}N(p,\alpha\gamma)^{12}C$ resonant nuclear reaction at a proton energy of 429 keV. This reaction was revealed by the specific 4.43 MeV γ-rays of the ^{12}C. In order to obtain an excitation curve at high resolution, the incident particle energy was increased by small increments starting from near-resonance energy. Voltage steps of 100 V were then applied to our new 2 MV tandem accelerator (Tandetron™) [13] for the $Ti^{15}N_x$ layers analysis. A pressure of 10^{-4} Pa was maintained during the analysis. A liquid nitrogen trap was mounted in front of the sample in order to reduce carbon contamination. γ-rays were detected in 4×4 in. NaI detector [14].

The excitation curves obtained depend on the natural width of the resonance (Γ_R), on the Doppler broadening (Ω_D), on the energy spread of the beam (Ω_B) and on the straggling effect (Ω_S) due to unequal energy loss of identical particles. In our case, the natural width ($\Gamma_R = 120$ eV) and the Doppler broadening ($\Omega_D = 90$ eV) at room

temperature are both well-known or easily estimated with the classical expression [11,15]. The beam energy spread was around $\Omega_B = 60$ eV on the basis of the accelerator specifications. The last parameter Ω_S corresponds exclusively to the energy loss in the nitride coating deposited on the substrate surface. In order to deconvolute the excitation curves and to extract the straggling part from the total excitation peak width, it has been assumed that all these contributions are gaussian-like [16]. This straggling value can be assumed proportional to the vertical expansion of the nitride, i.e., normal to the substrate surface. Furthermore, the height of the deconvoluted excitation yield can then be immediately correlated with the ^{15}N concentration in the layer probed by the proton beam and then to the lateral nitride coverage of the substrate surface.

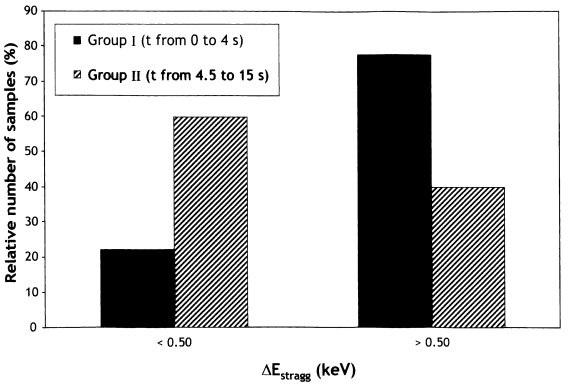

Fig. 1. Bar graph illustrating the relative occurrence of deconvoluted straggled energy width lower and greater than 0.50 keV for the group I sample (filled rectangle: deposition time less than 4 s) and for the group II (hatched rectangle: deposition time ranging from 4.5 to 15 s). These energy width values are extracted from the $^{15}N(p,\alpha\gamma)^{12}C$ excitation curves near 429 keV measured on $Ti^{15}N_x$ sputtered on low carbon steel ($p_{tot} = 0.20$ Pa, $p_{N_2} = 0.02$ Pa, $P = 11.7$ W /cm^2).

3. Results and discussion

It has been observed from the experiment that the straggling width varies from 0.30 to 0.62 keV for deposition time less than 15 s. Unfortunately, no apparent correlation of this can be found due to a possible surface contamination by carbon and oxygen or a beam instability. Nevertheless, the Fig. 1 has been plotted to illustrate the variation of straggled width (ΔE_{stragg}) for different deposition time (t). For the group I (nine samples with $t \leqslant 4.0$ s), the number of excitation yield curves with straggled width >0.50 keV is much more important than spectra with width less than this value. The inverse trend is observed on nitride from the group II (11 specimens deposited in 4.5–15 s). Furthermore, the mean value of straggling energy width equals 0.52 keV for the group I and 0.46 keV for the group II.

This decreasing trend starting from a relatively high value can be explained with an island (or Volmer–Weber) growth mode of the $Ti^{15}N_x$ on steel substrate [8,9]. In that case, the maximum nitride depth is immediately high and nitrogen atoms arriving on the surface create new clusters or aggregate with pre-formed island in 3D. The nitride depth probed by the proton beam remains roughly constant and equals the cluster mean height. After this first nucleation step (group I), the islands density saturates rapidly and the clusters tend to coalesce (group II). The mean depth decreases due to the filling of the void between the first nitride island. In other words, a better lateral coverage results in a lower average height of nitride probed by the protons.

The deconvoluted peak height of the γ-ray yield as function of the deposition time is shown in Fig. 2. Three regions divide these data. The samples of region I are characterised by a relatively low increase of the height proportional to the time. In the 3D growth mode (Volmer–Weber), it corresponds to a small extension of the cluster volume and to the increase of island density but between these clusters the substrate is still highly denuded. The next nucleation stage occurs for samples of region II where the coalescence reduces the island density to develop a cluster connected network with unfilled channels in between. During this step, the nitride coverage of the substrate surface increases rapidly as can be seen on region II of the Fig. 2. Finally, if $t > 15$ s (region III), the peak height of the yield reaches a maximum value corresponding to the bulk-like film concentration. The channels fill in and shrink, leaving isolated voids behind and the film becomes continuous but

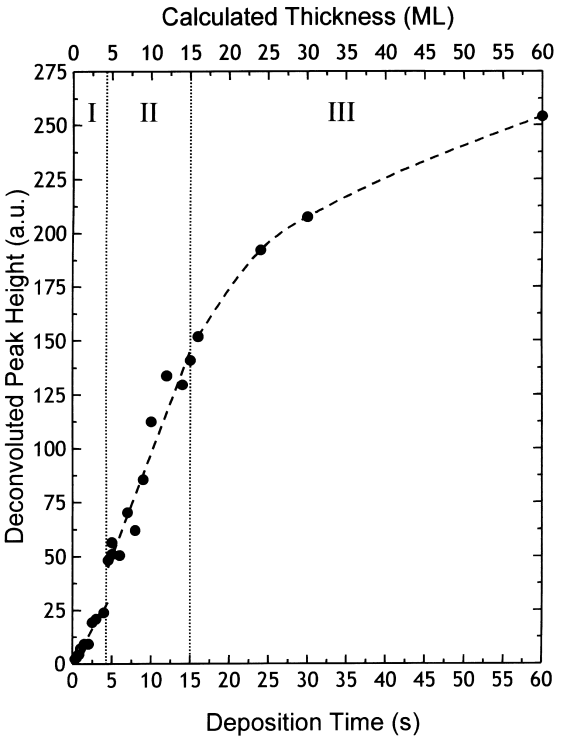

Fig. 2. Evolution of the deconvoluted peak height of the γ-ray yield measured by the nuclear reaction $^{15}N(p,\alpha\gamma)^{12}C$ near 429 keV on $Ti^{15}N_x$ sputtered on low carbon steel ($p_{tot} = 0.20$ Pa, $p_{N_2} = 0.02$ Pa, $P = 11.7$ W/cm^2) as a function of the deposition time ranging from 0.3 to 60 s. Estimated thicknesses from 0.3 to 60 ML are calculated with the deposition rate assuming a whole surface coverage. Three regions divide the figure, see text for details.

with in a porous structure. Many authors have detected that kind of columnar structure for low temperature TiN_x film on steel substrate [17]. It seems now that this columnar structure can be attributed to the strong 3D growth mode. Finally, it should also be noted that an island growth may be explained by the presence of preferential nucleation site on the steel surface such FeO (NaCl, $a = 0.431$ nm) with a very low lattice mismatch with titanium nitride [18].

4. Conclusion

Using a gas flow of isotopic nitrogen during deposition, it is possible to detect nitride coating of about 0.3 ML calculated thickness with $^{15}N(p,\alpha\gamma)^{12}C$ resonant nuclear reaction for 429 keV protons. The excitation curves obtained on nitride produced at various deposition times suggest an island growth mode giving rise to the usual columnar microstructure of sputtered $Ti^{15}N_x$ on low-carbon steel substrate. Unfortunately, it seems obvious that some uncontrolled parameters such as accelerator long time stability, substrate roughness and surface contamination could perturb the deconvolution procedure and prevent a quantitative growth study. Another growth study by conventional analytical techniques will complete these first results. Nevertheless, further work on the experimental setup and careful contamination control will improve the resonant nuclear reaction method. It is also likely that isotopic reactive gases will help the sputtered nitride and oxide process development in the near future.

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