Low grain size TiN thin films obtained by low energy ion beam assisted deposition

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Abstract

TiN thin films have been deposited on silicon wafers by electron beam evaporation of Ti with simultaneous assistance of nitrogen ion bombardment (IBAD technique). In order to reduce the oxygen incorporation in the films, a Ti pre-evaporation was done just before the deposition process. We have investigated the influence of the film thickness on both the structural and mechanical properties of the films. We found hard TiN films (of about 28 GPa) with very low film roughness (less than 3 nm for film thickness of 0.8 μm) and values for the grain sizes of roughly 20 nm as revealed by atomic force microscopy (AFM). Auger electron spectroscopy (AES) analysis was carried out to obtain the film stoichiometry showing almost pure TiN films with a very low content of oxygen (less than 2 at.%). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Titanium nitride; Hardness; Wear improvement; IBAD

1. Introduction

The study of TiN hard coatings is at present a subject of special interest, particularly with respect to their performance on tools for different applications, cutting, punching and shaping, mobile machine parts and also as decorative coatings on consumer goods. Apart from mechanical applications, this material is also extensively used in the micro-electronics, medical and aerospace industries. However, the presence of contaminants in the films, such as oxygen, can adversely affect their properties. The oxygen content in TiN materials is thus a critical parameter for its adequate performance in many industrial applications [1,2]. For example, oxygen contamination leads to an increase in the TiN film resistivity, which decreases the efficiency of metallic junctions in microelectronic devices [3].

Among the different techniques in use for deposition of TiN coatings, ion beam assisted deposition (IBAD) has received considerable attention, owing to its flexible controllability of the structural and chemical properties of the resulting films [4–11]. Films synthesised by the IBAD technique have improved adhesion to the substrate and corrosion resistance compared with coatings deposited without ion bombardment.

During the growth process of TiN films by different deposition techniques, coarsening of grains with increasing thickness of the deposited films is generally observed. Though the hardness of the films may also
increase, the coarsening effect leads, however, to a negative influence on the friction coefficient and hence on the wear properties. Therefore, in order to improve the performance characteristics of the films, it is important to analyse and optimise these two opposing effects.

In this work, we have focused our attention on the deposition of TiN films by IBAD. By varying the ion energy range (acceleration voltage) and dose (beam current), it is possible to control the properties of the deposited films and to obtain TiN coatings with optimised features. Therefore, this technique has allowed us to obtain coatings with improved mechanical characteristics that are discussed in terms of the film thickness, mean grain size and contamination levels.

2. Experimental procedure

2.1. Preparation of the TiN thin films

The deposition of TiN films was carried out by electron beam evaporation (APT&T EVM-5) of titanium with simultaneous bombardment of the growing film with a beam of nitrogen ions (see Fig. 1); also, a previous Ti pre-evaporation treatment was performed since it is generally assumed that Ti acts as an oxygen getter, thus reducing the oxygen level in the processing chamber [12,13]. A Kaufman ion source (type IBS-250) with a beam diameter of 3 in. was used. Different experiments were performed in order to study the influence of the deposition parameters, namely, the bombarding energy and the ion intensity. Optimum films (respective to film hardness) were deposited with an acceleration voltage of 350 V and an ion current of 15 mA. During the deposition, the pressure in the chamber was kept constant at $2.28 \times 10^{-4}$ Pa. The direction of the ion beam and that of the evaporated atoms (electron beam) was 45° and 10° to the normal of the substrate surface, respectively. The distance between the ion and electron beam sources and the substrate surface was 20 and 15 cm, respectively. In our experiments, TiN films were deposited on ⟨100⟩ oriented silicon substrates carefully cleaned, prior to the deposition process, in an acetone bath followed by an ethanol bath. In addition to this, and prior to film deposition, all substrates were subjected to a 5 min sputter-cleaning treatment with Ar+ ions. The deposition rate was optimised to 0.1 mm/min. The experimental conditions used in the present study are listed in Table 1.

2.2. Structural analysis and mechanical characterisation

A nitrogen to titanium content ratio of N/Ti = 1.1 was determined through X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) measurements performed in an ultra-high vacuum chamber with a base pressure of $3.8 \times 10^{-10}$ Pa and using a Perkin-Elmer ESCA/Auger spectrometer with double pass cylindrical mirror analyser (CMA). The AES data was acquired in the normal mode.

Table 1

<table>
<thead>
<tr>
<th>Experimental conditions</th>
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<td>Conditions</td>
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<tr>
<td>Background pressure (Pa)</td>
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<tr>
<td>Operating pressure (Pa)</td>
</tr>
<tr>
<td>Ion species</td>
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<tr>
<td>Ion beam flux (mA/cm$^2$)</td>
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<tr>
<td>Ion acceleration energy (keV)</td>
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<tr>
<td>Ion beam impinging angle (°)</td>
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<tr>
<td>Deposition rate (nm/s)</td>
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<td>Film thickness (nm)</td>
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kinetic energy of the incident electron beam was 3 keV with a total current of 33 nA. The XPS measurements were performed using Mg Kα radiation.

The film microstructure was observed by atomic force microscopy (AFM) measurements carried out under ambient conditions with a home-made microscope, as described by Kolbe [14]. Surface images were taken in the contact mode using sharpened silicon nitride cantilevers (Park Scientific Instruments and Olympus). The root mean square (rms) roughness values were obtained from different image sizes. Different areas of each sample were examined to check the uniformity of the films.

The hardness of TiN films was measured using nanoindentation techniques. For the measurements presented here, we used a Nano-Indenter® II (Nano Instruments, Inc.), with a Berkovich pyramid diamond indenter. The ac indentation technique was used for this investigation which was first introduced by Oliver et al. [15]. This technique allows us to measure continuously the hardness of the sample as a function of the indentation depth. The measurements were carried out at the maximum possible load in order to determine the effect of the substrate on the mechanical properties of the film.

Finally, the thickness of the deposited coatings on the silicon substrates were measured using a surface profiling system (Dektak 3030).

3. Results

3.1. Film composition

Fig. 2 is a representative AES spectrum of the TiN films (see conditions in Table 1) prepared in this work. The main peaks observed in the spectrum are nitrogen (383 eV) and titanium (417 eV). The titanium also gives rise to the low energy contribution together with a contribution that overlaps with the nitrogen peak at 383 eV. Furthermore, there are small contributions of argon (215 eV), carbon (272 eV) and oxygen (509 eV). Argon was implanted during the sputter cleaning process of the sample and it was used for energy calibration. Quantification of the TiN Auger spectra is complicated due to the overlap of the nitrogen KL_{2,3} L_{2,3} and titanium L_{3} M_{2,3} M_{2,3} transition peaks at 383 eV. In order to obtain the composition from the AES data presented in Fig. 2, a procedure according to Sundgren et al. [16] was followed. This leads to the following elemental composition of our films, Ar: 1.9 at.%, C: 2.3 at.%, Ti: 44.3 at.%, N: 49.6 at.% and O: 1.8 at.%.

The AES results have been confirmed by XPS measurements. Using tabulated photoionisation cross-sections [17], and electron mean free paths [18] and assuming an energy dependence of the analyser transmission function of the type 1/E_{kin} [19], we have obtained a nitrogen to titanium content ratio of N/ Ti = 1.1, which is in good agreement with the AES data.

As revealed by the X-ray diffraction analysis, the deposited TiN films are preferentially orientated in the (1 1 1) direction.

3.2. Microstructure and mechanical properties

The AFM images of the film surface taken at increasing deposition times reveal that the films grow uniformly with the deposition time. Sequential topographic images of the surface of the samples are shown in Fig. 3. The influence of the thickness on the morphology of the film is evaluated by measuring the mean grain size and the rms roughness of the samples. Table 2 shows the grain sizes of the films obtained from the AFM images (see Fig. 3). As can be observed, grain size values increase from almost 10 up to 25 nm for film thickness of around 0.8 mm. The rms
roughness along with the thickness of the films as a function of the deposition time are given in Fig. 4. As can be observed, the roughness of the surface abruptly increases in the first stages of the deposition process and then it keeps growing though more slowly. The rms roughness together with the mean grain size are represented in Fig. 5 as a function of the thickness of the film. We clearly see in Fig. 5 a growing trend both in roughness and grain size with increasing thickness.

The measurements of the film hardness yield values in the range of 24–28 GPa (see Fig. 6). The slight increase of the measured hardness values with increasing film thickness is mainly due to the decreasing influence of the Si substrate at higher film thickness.
4. Discussion

The grain size is of paramount importance in determining the strength of the deposited films. It has been demonstrated that in coatings without significant residual stress, a Hall–Petch relationship describes the increase in microhardness, $D_H$, with the inverse square root of the grain size (at constant film thickness)

$$D_H \propto d^{-1/2},$$

where $d$ is the grain size, and $K$ is a constant [20]. So, the low grain sizes observed in our films, which are below those generally reported in the literature for similar film thicknesses (~0.3 μm) [21], may explain the high hardness values (around 26 GPa) found in our work for thin films of TiN. These values are comparable with those obtained by Wittling et al. [22] using filtered cathodic arc deposition (FAD), once the substrate corrections are made.

It is worth noting that the reduction of the grain size brings about also a low rms roughness. Moreover, according to Müller et al. [1] an increase in the hardness of TiN films is observed when oxygen concentration in the chamber decreases. Therefore, although the present results are not yet definitive, the low oxygen content found in the films, possibly due to the efficient elimination of the oxygen content in the reaction chamber through the Ti pre-evaporation treatment, along with the small grain size observed in our films may have contributed, in a co-operative way, to the improvement of the TiN film hardness. This efficient oxygen-elimination might be behind the results reported by Müller et al. [1] on the behaviour...
of the hardness of TiN films with the ambient oxygen concentration and, indirectly, with those of Manory et al. [23] regarding possible mechanisms of TiN film wear improvement due to non-equilibrium treatments, i.e. post-deposition ion beam bombardment of TiN films previously deposited by IBAD. One of the main results by Manory et al. [23] is that, after post-deposition treatments with three different kind of ions (C⁺, N⁺ and Ar⁺), TiN films always showed reduced oxygen contamination together with significant improvement in wear performance. Therefore, our investigations suggest that both the low oxygen content in the TiN films and the small grain size obtained play a key role in the behaviour of the film hardness.

At present, we are investigating this effect (minimisation of oxygen content), and measuring the morphological properties of the films in order to assess the validity of the IBAD technique itself (without the need of post-deposition non-equilibrium treatments) for the preparation of TiN films with improved mechanical characteristics.

5. Concluding remarks

It has been demonstrated that TiN films with hardness values up to 28 GPa can be obtained using the IBAD technique with ion bombardment of relatively low energies (below 0.5 keV) and a Ti pre-evaporation treatment. The main structural property of these films is the small grain size of about 25 nm after reaching 0.8 mm film thickness. Both the small grain sizes and the low oxygen concentration (less than 2 at.%) found in the films lead to a hardness improvement of the deposited TiN thin films. Furthermore, the film roughness is very low (smaller than 3 nm for 0.8 mm thick films). These findings have been obtained for optimised TiN films with a N/Ti content ratio of 1.1 showing a {111} preferential orientation. Further research on the role played by the presence of minute amounts of oxygen on both the grain size and structural properties is now in progress.

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