Nano Indentation Inspection of the Mechanical Properties of Gold Nitride Thin Films

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ABSTRACT

The morphology and the local mechanical properties of gold nitride thin films were studied by atomic force microscope (AFM). Gold nitride films were deposited for the first time on silicon substrate without any buffer layer at room temperature by reactive pulsed laser ablation deposition (RPLD). The films were fabricated on (100) Si wafers by RPLD technique in which KrF excimer laser was used to ablate a gold target in N_2 atmosphere (0.1 GPa-100 Pa) and ambient temperature. Scanning electron microscopy (SEM) and atomic force microscopy inspections showed that the films were flat plane with rms roughness in the range of 35.1 nm-3.6 nm, depending on the deposition pressure. Rutherford backscattering spectrometry (RBS) and energy dispersion spectroscopy (EDS) used to detect the nitrogen concentration in the films, have revealed a composition close to Au_3N. The film's hardness, Young’s modulus, and scratch resistance were evaluated by nanoindentation and nanoscratch techniques in which AFM equipped with a diamond tip mounted on a metal foil cantilever was used to indent and scratch the film. Thus we were able to measure the mechanical properties along with the topography of the films characterization down to nanometer scale. Indentation and scratch measurements yielded hardness values of 2 GPa-3 GPa and a Young's modulus value close to 100 GPa.

The experimental data are processed according to Oilver and Phar theory and discussed in terms of grain size, boundaries and dislocation pinning.

Keywords: Thin film, Atom Force Microscopy, Nanoindentation, Nanoscratching.

1. INTRODUCTION

Significant efforts have recently been made to develop microelectronics and MEMS structures that include metallic contacts in micro-scale and nano-scales. Gold is the most frequently used element due to its exceptional combination of oxidation resistance and electrical conductivity. However, gold films are characterized by a very low hardness and there is a necessity of special alloying to enhance their mechanical properties. In this paper a preliminary study results of the mechanical properties such as hardness and Young’s modulus of gold nitride films deposited on Si substrates produced by reactive pulsed laser ablation deposition technique are reported. The RPLD method [1] offers many advantages over traditional techniques, such as low material consumption, short processing time and relatively low production costs. Moreover, the highly energetic plasma created by intense laser pulses in which the power densities are over the GW range, presents a great potentiality for the synthesis of new compounds, unattainable with the conventional thermal processes. With the RPLD technique it is aimed to obtain gold nitride layer which could improve film hardness, avoiding the use of metal pollutants, while still preserving the high electrical conductivity of pure gold films.

The ambient gas for nitride film deposition is usually molecular nitrogen, $N_{2.}$ Particular attention has been paid to the fabrication of titanium nitride films, which were the first to be deposited by RPLD following the high T_c superconductors [2]. A detailed review on RPLD of transition metal has been recently published [3].

The interest in gold nitride films arises from the fact that gold films are widely used as electric low resistance contacts in microelectronic industry. However gold films exhibit a low hardness about 2 GPa or even less therefore metals like Co, Ni, and Fe [4] or As, Pb and Ti [5] were often added to increase coating hardness. It was predicted that gold nitride layer could improve film hardness, and at the same time could avoid the use of metal pollutants, while still preserving the high electrical conductivity of pure gold films.

The first evidence of a gold nitride phase formation was obtained by irradiating an Au (110) single-crystal with nitrogen ions of kinetic energy 0.5 keV and 2 keV [6] and then detecting variations in the N 1s core level spectra by high resolution x-ray photoelectron spectroscopy (XPS). However annealing of nitrogen implanted surfaces up to 90 ^{o}C led to nitrogen desorption as was detected by the disappearance of the N 1s line, thus suggesting a low temperature limit for the gold nitride stability. Further studies on such samples were made employing synchrotron radiation photoemission spectroscopy etc [7]. The most likely stoichiometry was supposed to be Au_3N, since Ag and Cu form stable Ag_3N and Cu_3N phases, respectively. Recently, films containing gold nitride (~ 10.5%) were deposited on Si wafers by reactive nitrogen ion sputtering [8]. The films have exhibited an electrical resistivity of 11.9×10^{-8} Ωm at room temperature, as compared to the value of 2.2×10^{-8} Ωm of bulk gold.

In this work the characteristics of gold nitride films produced for the first time by RPLD technique are presented and discussed. During laser ablation high energetic neutral and ionic species are produced in the plasma plume, which can excite, dissociate and ionize the ambient nitrogen molecules thus producing a reactive environment, as shown and discussed in previous works on CN_x synthesis [9]. RPLD is the simplest procedure for new compound formation. Moreover, its perspective industrial applications are confirmed by the possibility to deposit films on large area and tri-dimensional substrates [10].

2. EXPERIMENTAL

Film deposition was performed in a stainless-steel high-vacuum chamber. Before each irradiation series the chamber was evacuated down to 2×10^{-5} Pa to remove any oxygen contamination.

A pure Au target was ablated by KrF (λ=248 nm) excimer laser pulses each of which length was ~30 ns. The pulse repetition rate was 10 Hz. The laser beam was incident on the target under an angle of about 45^{o}. The laser fluency-F, was set to 6 J/cm^2, to obtain a high-energy plasma plume in order to enhance the reaction processes. The target was rotated at a frequency of 3 Hz and vertically spanned during the ablation to obtain a smooth ablation procedure. The ablated material was collected on a (100) silicon substrates, placed at a distance of 40 mm from the target. The substrate was kept at room temperature during the deposition process where 1×10^4 laser pulses were used for each deposition. A dynamic flow of molecular nitrogen at pressures in the range p=0.1 Pa-100 Pa was maintained in the chamber during depositions. A pure gold film was deposited in vacuum (2×10^{-5} Pa) for reference.

The surface morphology of the films were characterized using JEOL 6300 SEM with energy dispersive X-rays spectroscope detector and a high resolution (<0.1nm) Digital Instruments DI 3100 AFM when operating in tapping mode while lateral resolution is limited by the curvature of AFM tip. The nanoindentation and nanoscratch tests were performed using cube corner diamond tips. The indentation depth in our experiments was no more 10% of the film thickness thus ruling out any substrate's effects on the measured data. The shape and condition of the diamond tip were characterized by scanning electron microscope before and after indentation, to eliminate any damage or tip contamination while sampling process. Only one indentation scheme of 5-5s (5s per load, 5s per unload) was used for all the different maximal loads.

Film's composition was calculated by computer simulation and data analysis of the experimental Rutherford backscattering spectra results [11]. Film's resistivity was measured and analyzed using the 4-point probe technique experimental results. Energy dispersion spectroscopy and X-ray photoemission spectroscopy techniques were also used to characterize and verify the deposited films chemical composition.

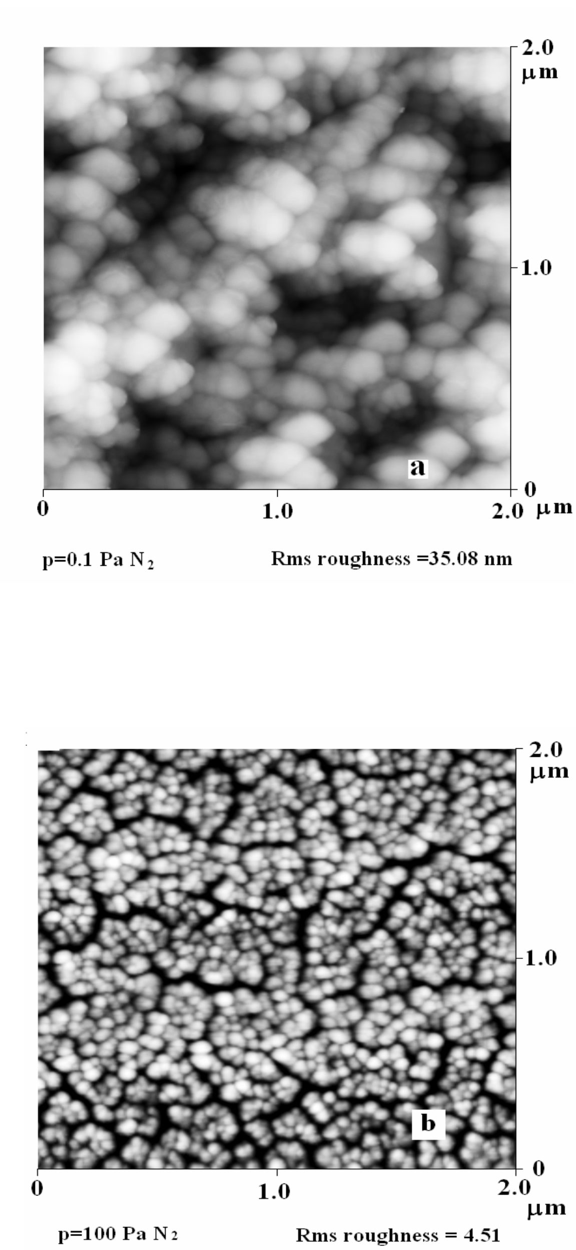


Fig.1 (a and b) AFM images of gold nitride films deposited at different pressure of N_2.

3. RESULTS AND DISCUSSION

For a naked eye inspection, the deposited films have the appearance of a yellow-gold coloured layers when prepared at low N_2 pressures (0.1 Pa-10 Pa), while exhibiting a yellow-green coloured layers at higher pressures. The colour variation is attributed to the film's thickness reduction, which decreases with increasing ambient pressure (see RBS results). SEM inspections of the film's surface have shown a characteristic smooth plane, without cracks or corrugations. A typical SEM micrograph is shown in Fig. 1 where fig 1a depicts a film produced in a N_2 partial pressure of 0.1 Pa and fig.1b shows a film ablated at N_2 partial pressure of 100 Pa.

Composition and thickness of the deposited films were inferred from RUMP simulations of the RBS experimental spectra [11]. The experimental RBS data of the laser deposited films were very well simulated yielding an accuracy of ~ 5% when assuming films formation with mean composition close to Au_3N and thickness in the range of 480 nm-550 nm for the lower N_2 pressures (0.1 Pa-10 Pa) and 200 nm-360 nm thickness for the higher N_2 pressures (50 Pa-100 Pa).

Electrical resistance of the deposited films measured with a four-point probe yielded a comparable value with the value of $2.6x10^{-8}$ Ωm, measured for the pure gold film which was deposited in vacuum. The resistivity increases to $4\text{-}5x10^{-8}$ Ωm for films deposited at 0.1 Pa-10 Pa and to $19\text{-}20x10^{-8}$ Ωm for films deposited at 50 Pa-100 Pa of N_2 partial pressures, thus indicating formation of films having a less conductive compound which is however still considered well above the typical conductivity needed for electrical contacts.

Formation of a nitride phase was confirmed by EDS and XPS measurements on some samples. EDS microanalysis have yielded a N/Au atomic ratio of 0.17 in samples prepared at p=50 Pa. This ratio increased to 0.19 after furnace annealing for 1 h and to 0.25 after annealing for 2 h at 250 ^{o}C. It is well known that quantitative element measurements with EDS are affected by a very large uncertainty. In any case, EDS measurements indicate that a quite large quantity of nitrogen is present in the films and that nitrogen is not purely physiadsorbed, since it does not decrease after prolonged annealing at 250 ^{o}C. The formation of a nitride phase was also confirmed by XPS in the spectrum of which the N 1s peak depicted in Fig. 2a is well evident around 400 eV.

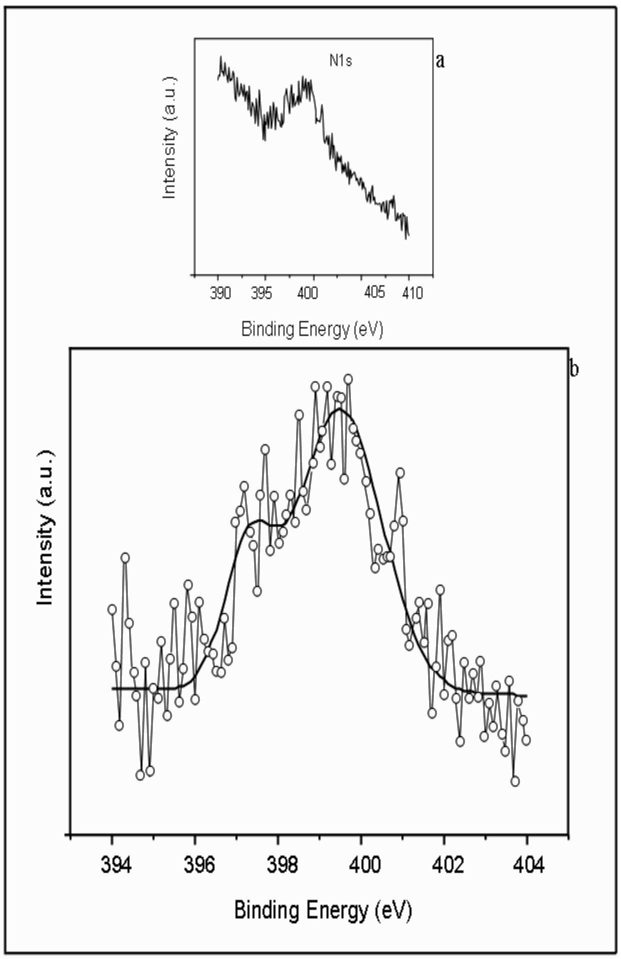


Fig.2 a) XPS spectrum of the film deposited at p=50 Pa N_2. b) The experimental curve is fitted by two Gaussians (full line).

The spectrum was acquired with a non monochromatic radiation so that the resolution is poor however the N1s peak is well fitted by two Gaussian curves centered at 397.3 eV and 399.5 eV. These values are very close to 396.7±0.2 eV and 397.7±0.2 eV for nitrogen bonded in nitrides as reported in Ref. 11. Since XPS signal originates from the few first surface layers, it is not surprising that the overall signal is a superposition of various components such as oxygen.

AFM investigations have clearly indicated a different surface topography for films prepared at low N_2 partial pressure (0.1 Pa-1 Pa) and for the ones prepared at high N_2 partial pressure (50 Pa-100 Pa), as obviously seen in Fig. 1a and 1b, respectively. In each case films appear to form a nanostructure feature. The rms roughness is much higher for films prepared in low N_2 ambient pressures as compared with high N_2 ambient pressure. In fact, it is 35.1 nm and 23.2 nm for films deposited at p=0.1 Pa and 1 Pa, respectively and decreases to 3.6 nm and 4.5 nm for films deposited at p=50 Pa and 100 Pa, respectively.

We use the nanoindentation method for mechanical properties evaluation of thin films at low loads developed by Oliver and Phar [12], in which depth-sensing indentation measurements produce a load-displacement curve from which the hardness and Young's modulus are calculated using :

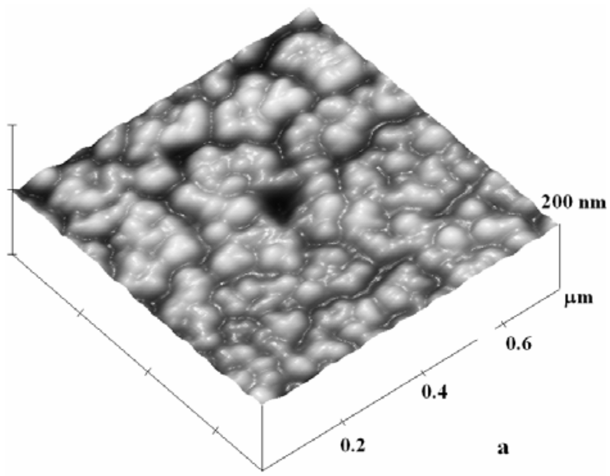
$$H = \frac{P}{A} \tag{1}$$

$$E_r = \frac{E}{1-\nu^2} = \frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A}} \tag{2}$$

$$\frac{1}{E_r} = \frac{1-\nu_{ind}^{\;2}}{E_{ind}} + \frac{1-\nu^2}{E} \tag{3}$$

Where P is the load, A is the projected contact area at that load and S is the elastic contact stiffness. E_r, E and ν are the reduced (measured) elastic modulus, the elastic modulus and the Poisson ratio for the tested specimen, respectively. E_{ind}, and ν_{ind} are the elastic modulus and Poisson ratio of the indenter respectively thus taking into account the indenter deformations during the indentation process. The indentation experiments were done on a selected flat region area free of precipitations.

The hardness of the films, as determined by nanoindentation, varies from 2 GPa to 3 GPa, as compared with the values of 0.64 GPa determined for bulk gold, 1.29 GPa for electroplated gold, 2.0 GPa for sputter deposited gold and 3.0 GPa-3.1 GPa for gold films with gold nitride deposited by reactive ion sputtering



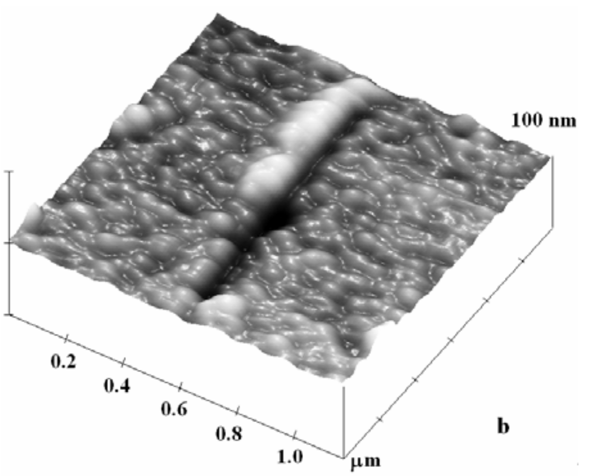


Fig.3 3-D images of gold nitride film deposited at p = 100 Pa of N_2.

a) nanoindentation (depth 16 nm)
b) nanoscratch (depth 21 nm)

[8]. The Young modulus is about 100 GPa, which is close to the values known for gold films in literature.

Nanoindent and nanoscratch images of the film deposited at p=100 Pa are shown in Fig. 3a and 3b, respectively. Scratching for load range of 10 μN to 100 μN and length varied from 0.5μm to 5μm were carried out by the same diamond tip used for nanoindentation. The scratch depth and width was used to evaluate the film scratch resistance. Surface profiles before and after scratching were obtained by scanning with the same diamond tip in the Tapping Mode of the AFM.

The mechanical response of the films (hardening vs. N_2 pressure) is open to speculation. It is well known that pure defect free metals are extremely ductile. Crystal defects such as grain boundaries, twins etc supply the strong obstacles needed to hold dislocation group and pin it down preventing any glide thus causing significant hardening of the material. A classical example of such behavior is the Hall-Petch relationship claiming that the hardness of the polycrystalline metal scales inversely proportional to the square root of the average grain size [13]. The mean grain size of gold nitride films decreases from 1780 nm^2 for p=0.1 Pa of N_2 to 670 nm^2 for p=50 Pa of N_2. That is, although the grains are small enough, they still differ in size approximately by a factor of two depends on the N_2 partial pressure.

The relationship between dislocation motion and plastic deformation can be used as an explanation basis for strengthening by grain size reduction. More experimental results are needed to get into detailed discussion of this issue.

4. CONCLUSIONS

Gold nitride films were deposited for the first time on Si substrate without any buffer layer at room temperature by reactive pulsed laser ablation. The deposited films were analyzed by Rutherford backscattering spectrometry X-ray photoemission spectroscopy and atomic force microscopy. Film resistivity was measured to be in the 4-20·10^{-8} Ωm range using 4-points probe technique. The hardness and Young modulus were obtained from nanoindentation and nanoscratch tests. The hardness of the films varies from 2 GPa to 3 GPa and Young modulus was found to be close to 100 GPa. Mechanical response of gold nitride films showed pressure dependence. The mean grain size of gold nitride films decreases from 1780 nm^2 (for p=0.1 Pa N_2) to 670 nm^2 (for p=100 Pa N_2).

5. REFERENCES

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