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Gold film with gold nitride—A conductor but harder than gold

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The formation of surface nitrides on gold films is a particularly attractive proposition, addressing the need to produce harder, but still conductive, gold coatings which reduce wear but avoid the pollution associated with conventional additives. Here we report production of large area gold nitride films on silicon substrates, using reactive ion sputtering and plasma etching, without the need for ultrahigh vacuum. Nanoindentation data show that gold nitride films have a hardness ~50% greater than that of pure gold. These results are important for large-scale applications of gold nitride in coatings and electronics. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1941471]

Metal nitrides often possess unique properties suitable for a number of applications, such as high hardness, high melting points, chemical stability, and useful magnetic and electrical properties. Gold films for use in the electronics industry[1,2] are deposited by electroplating and incorporate minute amounts of metallic and nonmetallic inclusions which can significantly affect bulk and surface properties.[3] Metals such as As, Pb, or Tl are typically added to increase the hardness of gold coatings[3] and there is a need to produce harder but still conductive gold coatings which reduce wear of the gold without the pollution associated with conventional additives. Although attempts to form gold nitrides have been recorded for the past 20 years, this compound was produced only recently, by Šiller and co-workers[4,5] by irradiating a single crystal Au(110) surface with low energy nitrogen ions in an ultra high vacuum (UHV) environment. Although these studies demonstrated the existence of a previously unobserved compound, it is not possible to measure many of the physical properties relevant to potential applications for films produced in this manner.

Here we present a scalable plasma-based process for the production of large area gold nitride films and the physical characterization of those films. The production of materials by plasma methods and/or ion bombardment is a delicate balance between implanting the ions in the surface and their removal by sputtering. Thus, low energy plasma conditions are essential for gold nitride to be formed.[6] Gold nitride films ~2 μm thick were deposited by reactive nitrogen ion sputtering directly on a standard 100 mm Si wafer for conductivity measurements, using an Edwards AUTO500 Magnetron sputtering system typically operating at 300 W power and with a bias voltage of 490 V. The pressure of nitrogen in the sputtering system was held at $\sim 5\times 10^{-3}$ mbar, yielding a deposition rate of ~0.2 nm/s.[6] The thickness of the films was measured by ellipsiometry. For hardness measurements, a ~200 nm thick layer of Ti was predeposited on the silicon surface by argon ion sputtering in order to improve adhesion of the gold nitride films to the substrate. Gold nitride was subsequently deposited to a thickness ~1.5 μm under the conditions described above. For comparison, pure gold films of the same thickness were deposited with argon ion sputtering.

We also investigated the physical properties of gold nitride films produced by exposing a pure gold surface to a nitrogen plasma. In this method, a gold film ~1 μm thick was deposited on a standard 100 mm Si wafer. The gold film was then transferred to a plasma etching system (STS, BOC Edwards sputter system). A surface gold nitride was then formed by exposing the gold film to a 13.56 MHz radio-frequency plasma for about 30 min. The power employed to generate the plasma was 300 W and the target biased to −240 V.[6] During this process, the nitrogen pressure in the plasma chamber was 6.4 mTorr, and the flow rate of N_2 was 50 cubic centimeters per second (sccm).[6] The plasma etching method produces nitride layers only ~30–50 nm thick, insufficient for hardness measurements. With reactive ion sputtering one can produce films of any thickness, hence this

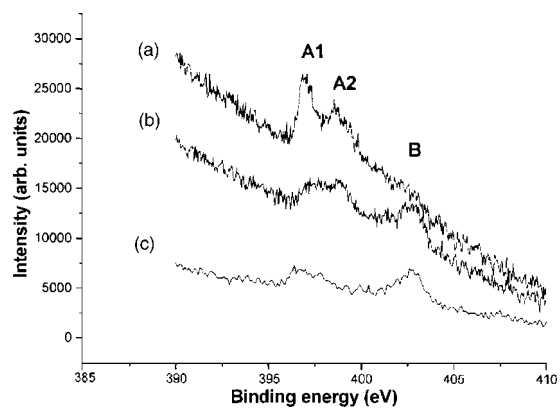

FIG. 1. N1*s* core level photoemission spectra obtained from (a) a thin film of gold nitride produced by nitrogen reactive ion sputtering, (b) a thin film of gold nitride produced by the plasma method, and (c) a Au(110) surface exposed to a nitrogen ion dose of 5770 μC cm^{-2} at 500 eV ion energy from Ref. 4. All spectra were obtained in normal emission geometry.

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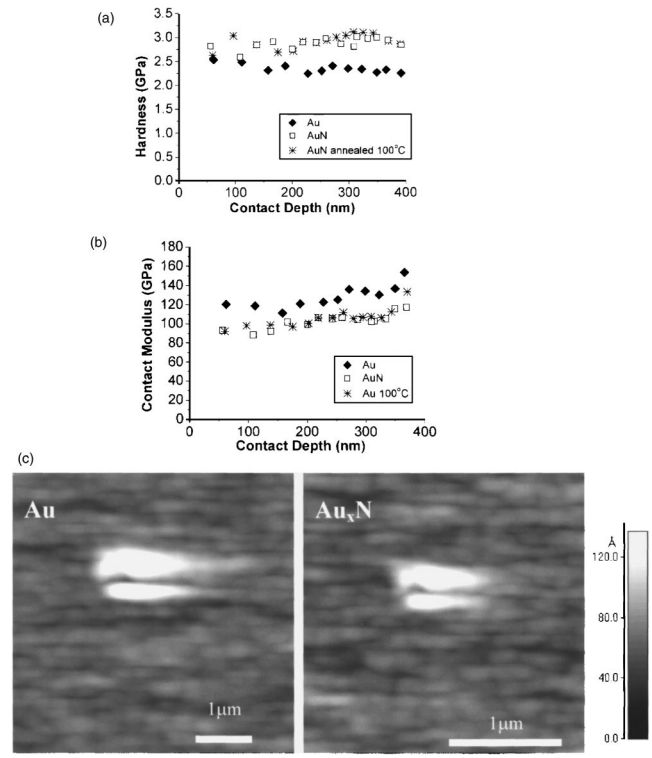

FIG. 2. Variation of (a) hardness and (b) contact modulus with contact depth determined by the method of Oliver and Pharr (Ref. 9) for gold, gold nitride, and gold nitride annealed at 100 °C (rhomb, squares, and triangles, respectively). The data presented are not influenced by the substrate. (c) AFM images of an indent in (a) gold and (b) gold nitride showing pile up and the need for correction of as-measured hardness and modulus values.

method was used to produce films for hardness measurements and for the conductivity measurements presented here.

In order to confirm nitride formation chemical analysis was performed with x-ray photoemission spectroscopy (XPS) at the National Centre for Electron Spectroscopy and Surface Analysis, Daresbury, U.K., using an ESCA 300 spectrometer and monochromated Al K_α radiation ($h\nu = 1486.6$ eV) at an overall resolution of 0.35 eV. In Fig. 1(a), we present an XPS spectrum of a gold nitride film produced by reactive ion sputtering and, in Fig. 1(b), by the plasma etching-based process. For comparison, a spectrum from gold nitride produced by ion irradiation of Au(110)[4] is shown in Fig. 1(c). Two distinct chemical states of nitrogen are observed in the N1*s* spectra shown. Peaks *A*1 and *A*2 are attributed to the formation of two gold nitride phases,[5] while peak *B* is associated with nitrogen molecules trapped in bubbles beneath the surface.[4,5] It can be seen that the signal from the nitrogen trapped subsurface (peak *B*) is smallest for the sample produced by reactive ion sputtering, possibly because bubble formation is less efficient under reactive ion sputtering due to higher erosion rates. The shape and binding energy positions of all peaks are almost identical leading to the conclusion that the larger scale process produces material of the same composition as observed previously for single crystal surfaces in UHV. Peaks *A*1 and *A*2 appear better resolved in Fig. 1(a) than in Fig. 1(b), which may be due to improved homogeneity and order in the former. The nature of the nitride phases formed during ion implantation was previously studied by *ab initio* theory.[5] Calculations predicted a triclinic Au_3N crystal structure which could be metallic. This phase is about 2.25 eV higher in energy than metallic gold and molecular nitrogen, and is thus metastable[5]—the reason why gold nitride has not been found in nature.

TABLE I. Hardness and contact modulii for the samples.

Sample	As-measured Contact modulus (GPa)	As-measured Hardness (GPa)	Pile-up corrected Contact modulus (GPa)	Pile-up corrected Hardness (GPa)
Sputter deposited gold	128±12	2.35±0.09	118±11	2.01±0.01
Au_xN	103±8	2.87±0.11	106±8	3.02±0.12
Au_xN (100 °C anneal)	106±10	2.92±0.16	110±10	3.17±0.17
Bulk gold			88±8	0.64±0.05
Electroplated gold			98±10	1.29±0.15

The percentage of gold nitride in the gold films investigated in this work (assuming the proposed stoichiometry of Au_3N[5]) is ~10.5%, and was determined from the ratio of Au4*f* to N1*s* photoemission peaks, corrected for photoionization cross section,[7] transmission of the ESCA 300 analyzer,[8] and electron escape depth. Here we present measurements of electrical conductivity and hardness of such gold nitride thin films prepared by nitrogen ion reactive sputtering and compare them with conductivity and hardness of pure gold films of the same thickness prepared by sputter deposition using an argon plasma. Mechanical measurements were made with a Hysitron Triboindenter fitted with a sharp diamond tip of cube corner geometry (~40 nm tip end radius), carefully calibrated using a fused silica standard by the method of Oliver and Pharr.[9] Twenty five indentations were made on each sample in a five by five array with a separation of five microns between each indent. Tests were performed at peak loads from 100 to 2500 μN under load control. Hardness and contact modulus E_r were initially determined from the load displacement curves produced using the methods of Oliver and Pharr.[9] The contact modulus is given by

$$\frac{1}{E_r} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}, \tag{1}$$

where E and ν are the Young's modulus and Poisson's ratio and the subscripts 1 and 2 refer to indenter and sample, respectively. Although the elastic constants of the diamond indenter are well known it is not possible to determine the Young's modulus of an unknown sample exactly unless the Poisson's ratio is known. For this reason the coatings tested in this study are characterized in terms of the contact modulus alone.

The Oliver and Pharr approach gives unreasonable results for these properties in gold due to the effects of pileup around the indentation.[10] To correct for this, the indent area

TABLE II. Calculated elastic properties of gold from single crystal parameters.

Property	Elastic modulus (GPa)	Poisson's ratio	Contact modulus (GPa)
Tensile	68.8	0.433	89
Hill average	78.5	0.423	88.2
Voigt average	88.1	0.414	97.3

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TABLE III. Apparent grain size of gold and gold nitride layers from AFM scans of the sample surface.

Material	Coating thickness (μm)	Grain size (μm)
Sputter deposited gold	1.5	0.39±0.12
Au_xN	1.5	0.25±0.13
Au_xN 100 °C anneal	1.5	0.28±0.12
Electroplated gold	17	5.8±0.7
Gold foil	200	150±15

was determined at the end of the test by atomic force microscopy (AFM) scans using the tip which made the indent.[10] For all coatings tested the hardness is approximately constant until the indenter penetration is greater than 25% of the coating thickness when the substrate starts to have an effect on the measured data and the hardness rises. This is similar to observations for other soft materials such as aluminium.[11] The uncorrected hardness of the gold is lower than that of the AuN whereas its uncorrected contact modulus is higher [Figs. 2(a) and 2(b)]. In Fig. 2(b) it appears that the modulus increases with indentation depth, this is because as the load increases the amount of pileup increases and hence the size of the correction to the hardness or modulus due to pileup increases (after correction, the modulii are constant with depth within experimental error). Annealing of the gold nitride has little or no effect on mechanical properties.

Considerable pileup of the films is visible in the AFM images of the indents [Fig. 2(c)] with the amount of pileup reduced for the AuN coating. The average hardness and contact modulus of the films before and after correction are shown in Table I. Within experimental error the contact modulus of gold and gold nitride is the same but the hardness of the gold nitride is about 50% higher. In comparison with gold electroplate and bulk gold the values for both hardness and contact modulus are higher. In both cases this is probably due to the small grain size of the coatings. For large grained material where the indent samples a single grain the measured contact modulus is usually close to the Hill or Voigt average for single crystal properties [Table II, with single crystal parameters $c_{11}=190$ GPa, $c_{12}=161$ GPa and $c_{44}=42.3$ GPa (Ref. 12)] as is observed for the bulk and electroplated gold coatings here. The hardness of the coating is critically dependent on its grain size, increasing as the grain size is reduced down to a certain limiting size, the so-called Hall–Petch behavior.[13] AFM measurements of the surfaces of the films tested in this study indicate that the grain size of the electroplated and bulk gold is much larger than the indentation size (Table III) but that the plasma deposited films have a much smaller grain size and the indentation will sample several grains. The hardness of the gold scales as the reciprocal of the square root of the grain size as might be expected for Hall–Petch behavior. In such circumstances film texture and the presence of grain boundaries can also have an effect on the measured contact modulus, particularly since elastic averaging methods are not reliable when only applied to material in a small number of grains.

In Fig. 3 we plot conductivity measurements made over a temperature range of 77 to 298 K for a 2.12 μm thick gold film with a ~10.5% gold nitride content, produced via reactive ion sputtering. The conductivity of the film was measured in the van der Pauw geometry.[14,15] thus eliminating any

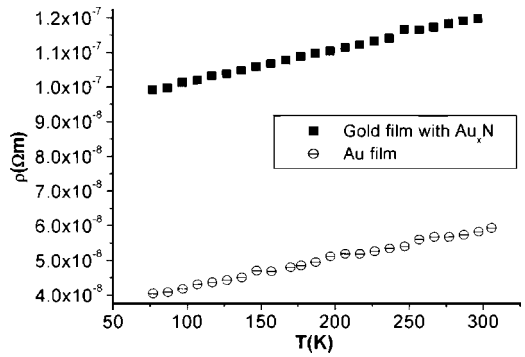

FIG. 3. Resistivity variation as a function of temperature for a 2.1 μm thick gold film containing ~10.5% gold nitride produced by reactive ion sputtering (squares). Resistivity dependence of a gold film, thickness 1.96 μm, over the same temperature range (circles).

contact resistance. For comparison we plot the resistivity of a pure gold film ~1.96 μm thick, over the same temperature range. In this way we find that the resistivity of the gold nitride film is $11.9\cdot10^{-8}$ Ω m at room temperature. Gold has a bulk resistivity $2.2\cdot10^{-8}$ Ω m (Ref. 16) at room temperature and this suggests that the film is still a metallic conductor.

The above results are significant because they demonstrate that gold films with incorporated gold nitride are harder than pure gold, but remain metallic, and confirm that gold nitride may be produced in large area films under conditions which may be readily scaled, an important factor for any large scale application.[1,2] Further studies are needed to optimize growth and increase the content of nitride in the film and consequently further increase the hardness.

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