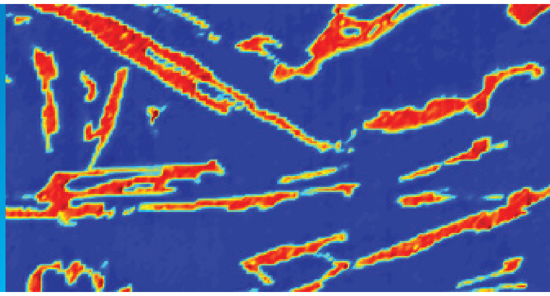
Effect of Annealing on 50nm Gold Films



Abstract

Ultra-thin gold films are used in many modern applications to impart essential optical qualities to surfaces. In this study, new nanoindentation technology, NanoBlitz 3D and Express Test, are used to evaluate the effect of annealing on 50nm gold films. Vacuum annealing for three hours (below 300°C) causes the hardness to decrease by 4.3% – 6.7% (99.9% confidence).

Introduction

Ultra-thin gold films impart essential optical qualities to many surfaces. Common applications include high-precision mirrors and magnetic storage media. For the gold film to fulfill its purpose over time, its microstructure and properties must remain stable through fluctuations in temperature and stress. The purpose of the present work is to use a new nanoindentation technique to assess how annealing affects the hardness of such ultra-thin gold films.

By virtue of its speed, NanoBlitz 3D and Express Test options for the KLA Nano Indenter systems dramatically improves our ability to detect significant difference when employing the Student's t-test to compare two measurement sets. Express Test is an advanced form of nanoindentation, performing one complete indentation every second. By contrast, typical nanoindentation technology requires at least 30 seconds per indentation. In other words, in a given time period, we can make 30 times the number of observations with NanoBlitz 3D and Express Test than with typical nanoindentation technology. This is important, because the value of the test statistic in the Student's t-test depends directly on the square root of the number of observations; that is, more observations increase the magnitude of the test statistic and therefore increase the likelihood of detecting significant difference, if in fact there is a real difference to be detected[1]. Thus, NanoBlitz 3D and Express Test can reveal small differences in hardness which may not be discernible with fewer indents. Because annealing may have only a slight effect—if any—on hardness, Express Test is an appropriate measurement tool.

Experimental Method

Four gold-film samples of 50nm thickness were tested. The set of four samples comprised identical films deposited on two different substrates and subjected to two different treatments. The first substrate was the bare wafer—a fine-grained fusion of titanium carbide (TiC) and alumina (Al2O3). Figure 1 shows a scanning-electron micrograph of the bare wafer. The second substrate was an alumina film, 2.6μm thick, sputter-deposited on the bare wafer. The first gold film (A) was deposited directly on the bare wafer, and the second (A') was the same film after vacuum annealing for three hours below 300°C. The third gold film (B) was deposited on the alumina basecoat, and the fourth (B') was that same film after vacuum annealing.

Equipment and Procedure

All samples were tested with a KLA Nano Indenter system, configured with the Express Test option. All tests were performed using a low-load transducer head fitted with a Berkovich indenter. In all, 400 indents were performed on each sample, with each indent performed to a maximum displacement of 20nm (40% of the thickness of the gold film). The testing protocol was purposefully designed to neutralize the effect of all physical variables that might influence the measured hardness other than the independent variable, which was annealing. Samples to be compared directly were mounted together on the same puck. Each sample was tested in multiple locations, and testing was systematically alternated between one sample and the other. The procedure may seem onerous, but it was necessary because four hundred independent observations yield extreme sensitivity, not only to the independent variable (annealing), but also to other uncontrolled variables. With four hundred observations on each sample, one can detect a significant difference of only 1% with 99.9% confidence, even if the standard deviation is 5%[2]. If four hundred observations were made at one site on one sample, followed by four hundred observations at another site on the other sample, one would likely discern a significant difference (according to the Student's t-test) on materials that were in fact identical, with the difference being due to some uncontrolled (and presumably unknown) variable. But we have found that the protocol followed in our experiment yields no significant difference on materials which are identical. Thus, when a significant difference is detected, we can safely conclude that it is due to the independent variable of interest.

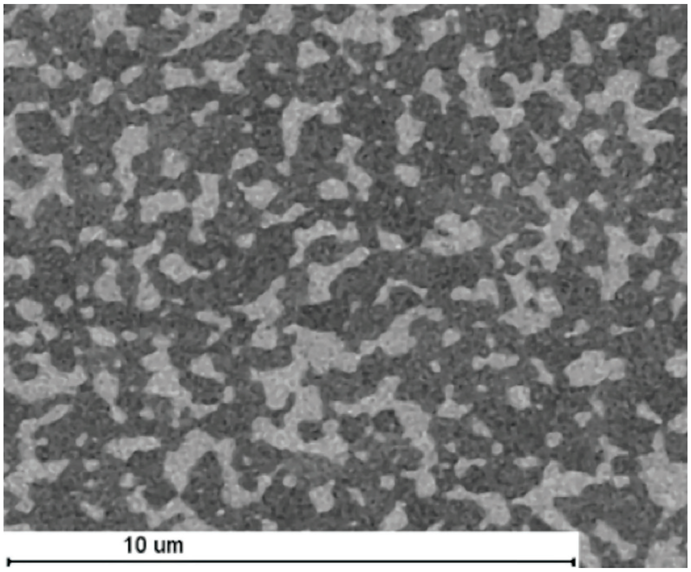


Figure 1. Scanning-electron micrograph of bare wafer. Titanium-carbide grains are light and alumina grains are dark.

Analysis

Sixteen sets of 25 indents were performed on each sample. For each set of 25 indents, the median hardness was calculated and reported as one observation. Thus, sixteen "observations" were made on each sample (N = 16). The Student's t-test was used to compare sample A with A' with 99.9% confidence by computing the mean hardness and standard deviation across the sixteen observations. We concluded that a significant difference in hardness exists if the following criteria is met:

$$\frac{|\overline{x_A} - \overline{x_{A'}}|}{\sqrt{\dfrac{\sigma_A^2 + \sigma_{A'}^2}{16}}} > 3.646,$$

where the right-hand side is the critical value for N = 16 with 99.9% confidence. The same analysis was applied to samples B and B'. The sensitivity of this analysis is not reduced by applying the Student's t-test to the 16 median hardness values rather than the 400 individual hardness values because the standard deviation across the 16 median values is much smaller than the standard deviation across the 400 individual values. Effectively, the 25 individual indents which make up one observation improve the precision of that observation. The Student's t-test evaluates the magnitude of the difference in means relative to the standard deviation.

Results and Discussion

Figure 2 shows the hardness for all four gold films. Annealing causes a slight but significant decrease in hardness. The hardness of the film deposited on the bare wafer decreased by 6.8% and the hardness of the film deposited on the basecoat decreased by 4.3%. These differences are so slight that detecting them with a high degree of confidence (99.9%) requires a large number of observations. By performing one indentation per second, the Express Test option allows such testing to be completed in an acceptable timeframe for industrial applications. The measured hardness for sample A is higher than that of sample B. This is probably not due to any difference in the gold films, but rather to their different substrates. In prior experiments, the hardness of the bare wafer was measured to be 28.48±0.61 GPa, and the hardness of the basecoat was measured to be 8.95±0.02 GPa. Given this large difference in substrate hardness, it is not surprising that we measure a higher hardness for sample A (which was deposited on the bare wafer) than for sample B (which was deposited on the basecoat). The difference in substrates may also explain the larger standard deviation for hardness measurements on sample A than sample B. The different materials in the bare wafer—alumina and titanium carbide — may influence hardness differently from indent to indent, with the net effect being a larger standard deviation. By contrast, the basecoat is a uniform layer of alumina whose influence on the film hardness ought to be uniform.

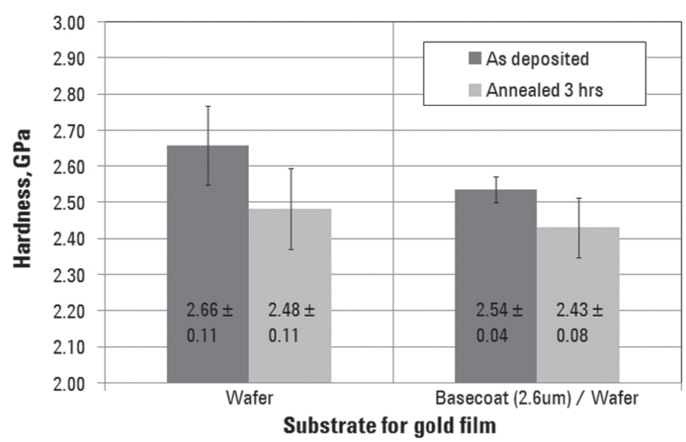


Figure 2. Hardness for four gold films. Annealing causes a slight but significant decrease in hardness (99.9% confidence).

Figure 3 is a histogram for one set of 25 indents. This set of 25 indents includes one aberrant test which returned a hardness of 0.17 GPa. This set clarifies the advantage of using the median rather than the mean to represent each set of 25 indents. The median of this set (2.37 GPa) coincides with the mode of the histogram, but the mean is lower (2.31 GPa) because it is skewed by the aberrant indent. NanoSuite or InView software allow allows the experimenter to easily filter out aberrant tests; if this aberrant test is excluded, the mean increases to 2.39 GPa. However, using the median to represent the set virtually eliminates the need for filtering by the experimenter (which may introduce bias) because the median is insensitive to the magnitude of the outlying measurement. In other words, an outlying hardness of -100 GPa has no more influence on the median than an outlying hardness of 1 GPa.

One of the most common questions about nanoindentation is "How thin of a film can you test?" The question is difficult to answer because it depends, among other things, on surface roughness and the degree of mismatch between film and substrate properties. Raw measurements of force and displacement are accurate to within less than a nanometer and less than a micro Newton, respectively. But accurate determination of mechanical properties depends on more than just the accuracy of force and displacement. Specifically, the geometry of the contact must be well known and the influence of the substrate must be either small or well understood. This work clarifies conditions under which ultra-thin films can be tested. We obtained accurate and useful results on these 50nm gold films because (1) the films were atomically smooth, (2) hardness is relatively insensitive to substrate influence and (3) we were more interested in the change in hardness due to annealing than the absolute value of hardness.

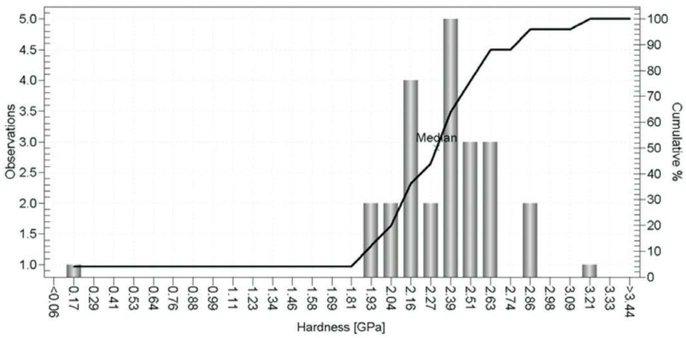


Figure 3. Histogram of one set of 25 indents on sample B'. The median is 2.37 GPa; The mean (2.31 GPa) is affected by one aberrant indent (H = 0.17 GPa). Histogram is automatically generated by NanoSuite or InView software.

Conclusions

A new nanoindentation technology, Express Test, was used to discern a small but significant decrease in the hardness of 50nm gold films due to annealing. Because the decrease in hardness caused by annealing was small, many indents were required in order to discern it with a high degree of confidence (99.9%). By performing one indentation per second, Express Test allowed many indents to be performed in a reasonable timeframe. However, these indents had to be carefully planned in order to neutralize the influence of all other physical variables except the independent variable (annealing). Specifically, each sample was tested in multiple locations, and testing was alternated between one sample and the other.

References

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2. Hay, J., How much indentation testing is enough testing?, Keysight Technologies, 2014, Document No: 5991-2145EN, Date Accessed: July 16, 2013; Available from: http://literature.cdn.keysight.com/litweb/pdf/5991-2145EN.pdf.

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KLA Corporation
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Milpitas, CA 95035
www.kla.com

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