Mechanical Properties Measurement of Nanowires Anisotropic Conductive Film by Nanoindentation Technique

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ABSTRACT

As microelectronic packaging industry grows explosively, high I/O density interconnects and reliable packaging design are recognized as the main concern of the IC packaging industry. Hence, in this investigation, a novel type of anisotropic conductive film (ACF) composed of cobalt nanowires and polymer was developed and used in place of conventional solder bumps for ultra-fine pitch interconnect. Unlike some other ACF materials that blend either nanowires, tubes, or powders in polymer, the nanowires entrenched in polymer is well aligned in one direction so as to achieve high anisotropic conductance. Basically, the material properties of the nanowire/polymer-based conductive film would have a great effect on the thermal-mechanical behaviors of the technology, which would generally lead to a reliability issue. Thus, the underlying goal of the study was to characterize the out-of-plane mechanical properties, including reduced modulus and hardness, through a nanoindentation technique. The tip of nanoindentation was 300nm in diameter and measured method was force-control.

Results show that the mean value of the reduced-modulus of the film is 14.471GPa at a standard deviation of 2.578GPa. These statistical results were based on 102 data points with high consistency.

Keywords: cobalt nanowires, nanoindentation, reduced modulus, hardness, AFM.

1 INTRODUCTION

Up to now, numerous types of advanced microelectronic packaging technologies have been developed to reduce package size, improve I/O density, and achieve higher thermal performance, etc. In order to attain high I/O density, fine pitch interconnect has became one of the main concerns in electronic packaging design. The traditional flip chip interconnect technologies, such as solder bumps, have limitation in achieving high I/O requirement due to that the fine pitch solder bumps could be bridged together during the soldering process. Therefore, in order to fulfill the demand of ultra-fine pitch interconnect, a novel flip chip packaging technology that adopts a cobalt nanowire/polymer-based conductive film was developed by Electronic Research & Service Organization / Industrial Technology Research Institute (ERSO/ITRI). The nanowire/polymer-based conductive film was designated as interconnect between silicon chip and substrate. Prior to its application in electronics devices, characterization of the reliability of the technology is of great importance. It should be further noted that the packaging reliability is strongly dependent of the mechanical behaviors of components, which are mainly determined by the associated mechanical properties.

Among the diversified packaging components, the nanowire/polymer-based conductive film plays a key role in affecting the thermal-mechanical behaviors of the technology, and thus, deserves an extensive assessment of its mechanical properties. However, the film contains millions miniature nanowires with nanoscale in diameter and microscale in length, and thus, imposes a great challenge in the characterization of its bulk mechanical properties through traditional extraction techniques. In the study, we attempted to explore the out-of-plane mechanical properties of the anisotropic conductive film by means of a nanoindentation technique. During the measurement, the indented shape and the surface roughness of the conductive film were visualized by an atomic force microscope (AFM). The nanowires were fabricated by electro-depositing cobalt alloy in an anodic aluminum oxide (AAO) template based on the template assisted nanowire growth technique. Next, after the removal of AAO template, the trenches among the fabricated highly-aligned nanowire array were then filled in with low viscous polymer. Low viscous polymer was then spread over and filled into the gap of pillar-like cobalt nanowire array after surface treatment by oil-acid. Laser ablation was then used to remove the excessive polymer covering the tip of nanowires. A Hysitron Tribiscope nanoindenter with Berkovich diamond nanoindenter tip was used to take images of the measured object and furthermore, to perform nanoindentation tests. To ensure a reliable experiment result, more than 100 randomly-selected sampling points on the surface of the ainsotropic conductive film were performed to extract the associated data. During the measurement, the reduced modulus and hardness data were recorded and analyzed through statistical methods.

2 EXPERIMENTATION

2.1 Fabrication of Nanowires Anisotropic Conductive Film

The fabrication process flow of nanowires conductive film was shown in figure 1. The AAO templates were purchased from Whatman and the diameter and thickness of nano-pores was about 200nm and 60 um. Before electro-deposition, a thin Cu seed layer had to be deposited onto one side of AAO for electric conduction. The cobalt was then deposited into the nanopores of AAO with magnetic alignment. The cobalt nanowires were deposited from the plating solution composed of 252g/l $CoSO_4.7H_2O$, 7g/l NaCl and 50g/l boric acid. After removal of AAO by 5% NaOH aquous solution, the low viscous polyimide was spread over nanowires to fill into the channels between nanowires under magnetic field. In order to make the polymer flow into the nanowires forest, the surfaces of nanowires have to be hydrophobilized by fatty acid to increase the capillary force between polymer and nanowires. After curing, the polymer film containing nanowires was obtained. Laser ablation was then used to remove the excess polymer covering the surface of nanowires composite film until the tips of nanowires shown up.

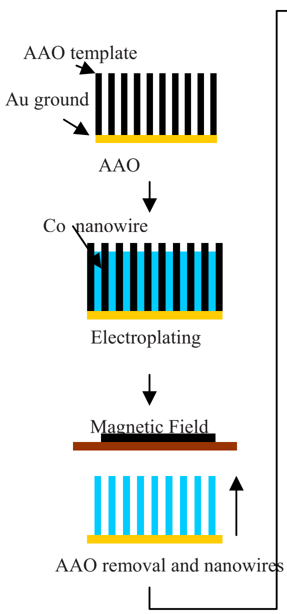


Fig. 1. Process Flow of Nanowires Conductive Film

Figure 2 shows the SEM pictures of nanowires anisotropic conductive film with 30 um in thickness, after laser ablation and mounting on a silicon substrate with 600um in thickness for nanoindentation purpose. The surface roughness of cobalt nanowire/polymer-based conductive film was controlled with high uniformity, and the polymer was well-filled into the space between each nanowires without bubble or crack which could affect the measurement results.

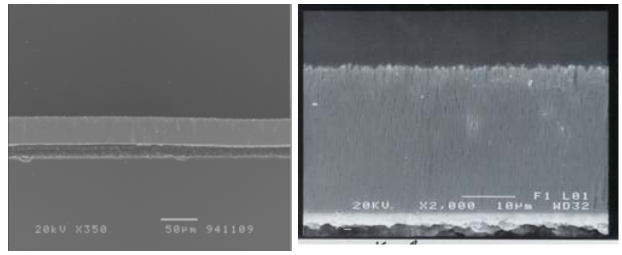


Fig. 2. (left) SEM image of side view of nanowires anisotropic conductive film (right) enlarged view of polymer filling

2.2 Nanoindentation

In this investigation, a Hysitron Triboscope nanoindenter in conjunction with AFM was used to perform indentation tests and imaging. The nanoindenter with three-sided pyramidal (Berkovich) diamond tip monitored and recorded the load and displacement during indentation with a force resolution of about 1nN and a displacement resolution of about 0.2nm. The samples were put on a horizontal sample holder as shown in figure 2. The optical microscope was used to image the sample and then indent the selected area defined by optics. Post-test imaging provided the ability to verify that the test was performed in the anticipated location and reliable data. Before experiment, the shape function of indenter tip was calibrated by a standard quartz specimen. The area function is related the projected contact area (A) and the contact depth (hc) as equation (1).

$$A\left(h_c\right)=C_0h_c^2+C_1h_c+C_2h_c^{1/2}+C_3h_c^{1/4}+C_4h_c^{1/8}+C_5h_c^{1/16} \quad (1)$$

The calibration is based on the assumption that modulus were elasticity, constant, and independent of indented depth. For the ideal shape function of Berkovich tip, the C0 should be 24.5. In this experiment, a series of indents at various indented depths were conducted for calibration purpose and the results of coefficients of shape function was fitted as follows, C1=2.919e2, C2=3.6167e4, C3=-1.2474e5, C4=-1.1948e5, and C5=2.4147e5.

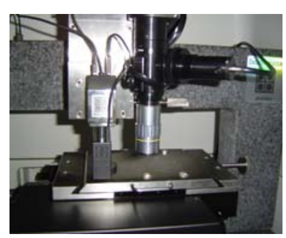


Fig. 2. Nanoindentation experiment setup

After the indentation projected area calibration, the hardness and reduced modulus were calculated from the load-displacement data. The reduced modulus was calculated by Oliver-Pharr data analysis procedure. The initial contact stiffness can be obtained from the slope of the initial portion of the unloading curve as

$$S = {dP}\Big/{dh} \tag{2}$$

where h is the function of contact area. The equation (2) can be rearranged as follows:

$$S = \frac{2\sqrt{A}}{\sqrt{\pi}} E_r \tag{3}$$

where E_r is the reduced elastic modulus that accounts for the compliance of the sample and of the indenter tip. The E_r can be given as springs in serious as follows:

$$\frac{1}{E_r} = \frac{1-\nu_i^2}{E_i} + \frac{1-\nu_s^2}{E_s} \tag{4}$$

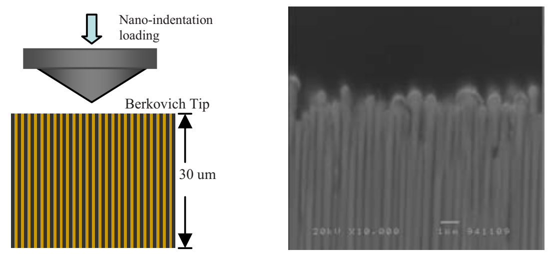
where E and ν are the elastic modulus and Poisson's ratio, and i and s refer to the indenter and sample respectively. In this experiment, the material of indenter tip is diamond which $E_i = 1141GPa$ and $\nu_i = 0.07$. The hardness was obtained as

$$H = {P_{\max}}\Big/{A} \tag{5}$$

where $P_{\max}$ is the maximum indentation load and A is the projected contact area at the peak load.

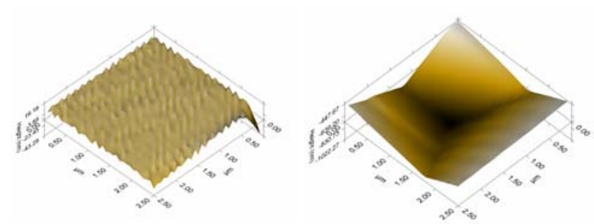
3 RESULTS AND DISCUSSION

The cobalt nanowires were fabricated by electroplating and PI was used as matrix material providing lateral support and enhancing the overall mechanical strength. The dimensions of cobalt nanowire/polymer-based conductive film were 30 um in thickness, and 1 cm in diameter. Each nanowires were 200nm in diameter, and 20 nm in spacing. Figure 3 (a) illustrates the nanoindentation experiment using Berkovich diamond nanoindenter tip. SEM was used to examine the surface roughness of the cobalt nanowire/polymer-based conductive film and the results is shown in figure 3 (b). The SEM image showed that the nanowires were presented in a vertically-aligned forests and the surface roughness of nanowires was less than 1 um. The in-situ indents were made under force control mode and the peak nanoindentation depth was approximate 1 um, which is far less than 30% of the film thickness based on a general empirical rule. Therefore, the substrate effect on the measurement of the hardness and reduced modulus can be ignored. Indents were repeated over 100 times at randomly selected location and the indentation configurations were imaged immediately after the indentation test using the same tip. Figure 4 (a) shows the 3D AFM image of the surface of cobalt nanowire/polymer-based conductive film. The tips of nanowires were vertically emanated from the surface of cobalt nanowire/polymer-based conductive film which is exactly consistant with the SEM picture shown in figure 3 (b). Figure 4 (b) shows the scaned image from the AFM after indent. It canbe noticed from the scan that the nanowires cannot be observable around the indented area.



(a) (b)

Fig. 3. (a) Schematic of nanoindentation experiment; (b) SEM image of vertically aligned nanowires



(a) (b)

Fig. 4. (a) 3D AFM image of the surface of nanowires conductive film; (b) 3D AFM image of indented area

The initial unloading slope was fitted to the power-law relation, and, combining shape function, the stiffness, reduced modulus, and hardness can be obtained using Oliver-Pharr method. Figure 5 and figure 6 show the reduced modulus and hardness of cobalt nanowires conductive film, respectively, obtained from 102 data points. The range of reduced modulus of cobalt nanowires film was from 10GPa to 20GPa and the range of hardness was from 0.1GPa to 0.27GPa. The mean value and standard deviation of reduced modulus were 14.471GPa and 2.578GPa, respectively. The mean value and standard deviation of hardness were 0.173GPa and 0.048GPa listed in table 1.

The results such as reduced modulus and hardness obtained from this investigation were much smaller than bulk material calculating by rule-of-mixture theory. However, almost all material properties from references were obtained without considering size effect, defects and fabricating process induced changes of material properties. In this investigation, the interfacial adhesion strength between electroplated cobalt film and PI was measured by pull test. The test results (Sample: Si/Ti/Cu/PI; adhesion: 70MPa, failure occurred on interface between Si and Ti) shown that the interfacial strength was strong between cobalt and PI, and thus, the possibility of weak interfacial strength induced low modulus was not existed. Also, there was no obvious void or micro crack in cobalt nanowires conductive film examined by SEM image. Thus, the most possibility that caused low reduced modulus and low hardness was nano-defect of cobalt nanowires. Therefore, further research is needed to investigate the relation between mechanical properties and single nanowires with various kinds of defects.

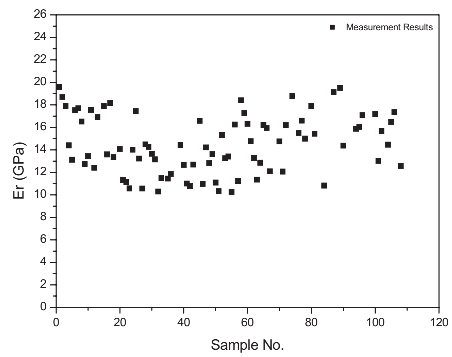


Fig. 5. Reduced Modulus

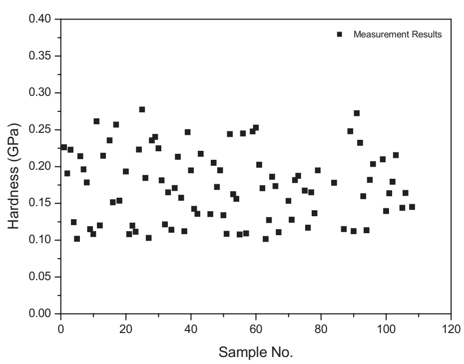


Fig. 6. Hardness

	Mean	Stand Deviation
Reduced Modulus (GPa)	14.471	2.578
Hardness (GPa)	0.173	0.048

Table 1: Statistical analysis of mechanical properties measurement results

4 CONCLUSIONS

In this investigation, the mechanical properties of cobalt nanowires anisotropic conductive film fabricated by electroplating were measured by nanoindentation technique and the measurement results including reduced modulus and hardness were reported in this paper. The mean value of reduced modulus is 14.471GPa and the standard deviation is 2.578. The reduced modulus of nanowires conductive film was smaller than bulk material calculating by rule-of-mixture theory; however, defects and size effect were not considered in the theory. Thus, more effect is needed to capture the relation between mechanical properties and nanowires with various kinds of defects in the further research.

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