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Study of the Middle Layer Effect of Multilayered Coatings
中間層效應對多層薄膜的影響之研究

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Abstract

In this paper, the middle layer effect of multilayered coatings on nanoindentation with Berkovich probe tip was investigated with the finite element analysis. Firstly, the bulk material Si and the Ti, Cu and Cr films on Si substrate (i.e., Ti/Si, Cu/Si and Cr/Si) were conducted with a high-resolution nanomechanical test. The Young's modulus of the bulk material Si and Ti, Cu and Cr films can be obtained by using the Oliver and Pharr method [1]. Moreover, based on the elastic-perfectly plastic material model, the finite element method was employed to determine the yield stress of all thin films and the bulk material Si. Secondary, multilayered coatings with different thickness and different material (i.e., Ti/Cu/Si and Ti/Cr/Si) of the middle layer were conducted by nanoindentation and simulated by finite element analysis. Finally, the results showed that comparison of the experimental data and numerical results demonstrated that finite element approach is capable of reproducing the load-depth curves of nanoindentation test at multilayered coatings problems. Furthermore, it is concluded that the lager thickness of soft middle layer material is the softer surface film response, and the harder middle layer material is the harder surface film response.

Key Words: Middle Layer, multilayered coating, nanoindentation, and FEM

摘　要

本文使用貝克維奇探針的奈米壓痕儀實驗和有限元素法來探討中間層效應對多層薄膜之影響。文中首先利用奈米壓痕儀實驗與奧利弗-華爾法求得矽基材與薄膜鈦、銅、鉻分別鍍在矽基材上的楊氏係數。然後假設薄膜為彈完全塑性材料，再利用有限元素法分別求得個基材與薄膜的降伏強度。接著利用有限元素與實驗方法，詳加分析不同材質與不同厚度的中間層，對多層薄膜的影響。結果顯示，數值分析與實驗所得非常接近，因此有限元素法有能力分析此問題。同時得到，軟的中間層材料厚度越厚，則表層薄膜變形越大。反之，若中間層材料越硬，則表層薄膜變形越小。

關鍵詞：中間層、多層薄膜、奈米壓痕儀及有限元素法

1. Introduction

It is well known that the mechanical surface properties of many materials can be improved by depositing nano- and micro-scale an appropriate thin film for many applications. [2-5] Because the deformation of coated surfaces produced by tribological interactions can result in substantial damage, it is very important to quantify the resistance of the material to such damage. For this reason the evaluation of the mechanical properties of thin films or multilayered coatings is of fundamental importance. An accurate determination of surface properties is critical to understand for a variety of effects on component performance. Due to the micro- and nano-scale of the interested surface, nanoindentation provides a feasible approach to study mechanical surface properties of many materials at pertinent scale.

Multilayered coatings have attracted attention in both scientific and commercial research in electronics, optical devices and tribological protection applications for many years because they can combine two or more different components for a special purpose. Wen et al. [6] used X-ray diffraction, transmission electron microscopy, and nanoindentation to investigate the microstructure, hardness and elastic modulus of Ag/Co multilayers. It results showed that all the multilayers have well compositionally modulation structure. Chen et al. [7] used X-ray diffraction, scanning electron microscopy, typical secondary ion mass spectroanalyzer, nanoindentation, and scratch test to study the microstructure and mechanical properties of gradient Ti (C,N) and TiN/Ti (C,N) multilayer PVD coatings. It results showed that the gradient Ti (C,N) and TiN/Ti (C,N) multilayer coating exhibit higher nano-hardness compared with homogeneous TiN coating. Gradient Ti (C,N) and TiN/Ti (C,N) multilayer coatings exhibit better adhesion with the substrate compared with homogeneous TiN coating.

Since experimental approach to study the effects of surface integrity and mechanical surface properties of material is time consuming and tedious due to the very fact of difficulty to prepare test specimens. Finite element (FE) analysis provides a convenient method to simulate a nanoindentation process with the influences of concern factors. Due to the obvious mathematical complexity to analyze the nanoindentation process, the finite element is an important role in recent technology developments and has been proved as a powerful tool in the nanoindentation simulation. Lichinchi et al. [8] used FEM to simulate nanoindentation of TiN film on HSS by using a commercial finite element code ABAQUS, and both axisymmetric and three-dimensional models were employed. They compared the experimental load-depth curves of titanium nitride thin film on high speed steel substrates with numerical results. Successively, they studied the effect of substrate on the hardness measurement and concluded that both models are similar and provide good fit. Ma et al. [9] employed the finite element method for elastoplastic large strain to simulate the indentation test for Al film on Si substrate, and a hybrid method was presented to determine the mechanical properties of the films by combining calculation with nanoindentation test. Bai et al. [10] used the finite element method to simulate the nanoindentation process. The effect of internal stress on hardness and elastic modulus was investigated by nanoindentation simulation with the FEM. The experiment results and calculation results were further explained by contact mechanics analysis. Pelletier et al. [11] have investigated the influence of material bilinear elastic-plastic behaviour model for numerical simulation of nanoindentation testing of various bulk metals. They employed an axisymmetric rigid cone and equal volume to the Berkovich pyramid indenter to simulate the test. The indenter and the specimen were treated as a revolution body in order to have three-dimensional situation. The numerical simulation results of loads versus displacement compare reasonably well to experimental results of nanoindentation tests of pure metals such Fe, Ni, Ti and A316L and TAFe alloys. However, they concluded that different pairs of yield strength and plastic modulus can produce a good fit to the experimental results of load versus displacement. Their explanation for this non-uniqueness of solution would be the bad definition of the indenter geometry and the adopted material behavior.

In the literature, we found the mechanical properties of single layer or multilayer films on nanoindentation were investigated frequently, but the middle layer effect of multilayered coatings has never been studied. In this paper, the middle layer effect of multilayered coatings on nanoindentation with Berkovich probe tip was investigated with the finite element analysis. At first, the bulk material Si and the Ti, Cu and Cr films on Si substrate (i.e., Ti/Si, Cu/Si and Cr/Si) were conducted with a high-resolution nanomechanical test, the Young's modulus of the bulk material Si and the Ti, Cu and Cr films can be obtained by using the Oliver and Pharr method. Moreover, based on the elastic-perfectly plastic material model, the finite element method was employed to determine the yield stress of the bulk material Si and all thin films ((i.e.,Ti, Cu and Cr). In addition, multilayered coatings with different thickness and different material (i.e., Ti/Cu/Si and Ti/Cr/Si) of the middle layer were conducted by finite element analysis.

2. Nanoindentation

The bulk material, single layer or multilayer films as studied with a high-resolution nanomechanical test instrument which is a nanoindenter (Triboscope, Hysitron) assembled on an atomic force microscope (Autoprobe,

CP-Research), and a three side pyramidal Berkovich probe tip is used in the test. Five indentations were made in each sample at the same maximum loads. Nanoindentation is performed under a precisely continuous measurement of the load and the depth during the test. Fig. 1 shows a schematic draw of an indentation load via depth curve.
In the Oliver and Pharr [1] method, the hardness H and the reduced modulus E_r are derived from

$$H = \frac{P_{\max}}{A} \tag{1}$$

and

$$\left(\frac{dP}{dh}\right)_{unload} = S = 2\beta E_r \sqrt{\frac{A}{\pi}} \tag{2}$$

where $P_{\max}$ is the maximum indentation load, A is the projected contact area, S is the unloading stiffness measured at maximum depth of penetration h, β is a constant that depends on the geometry of the indenter for Berkovich indenter $\beta = 1.034$. The reduced modulus is used in the analysis to take into account that elastic deformation occurs in both the indenter and the specimen and it is given by

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \tag{3}$$

where E , E_i and ν ν_i are the elastic modulus and Poisson's ratio of the indenter and the specimen material, respectively. For evaluating the elastic modulus E_r, the slope $\left(\frac{dP}{dh}\right)_{unload}$ and the contact area A should be determined precisely. A least mean square fit to 90% of the unloading curve is made according to the hypothesis that the unloading data will be expressed by a power law

$$P = P_{\max}\left(\frac{h - h_f}{h_{\max} - h_f}\right)^m \tag{4}$$

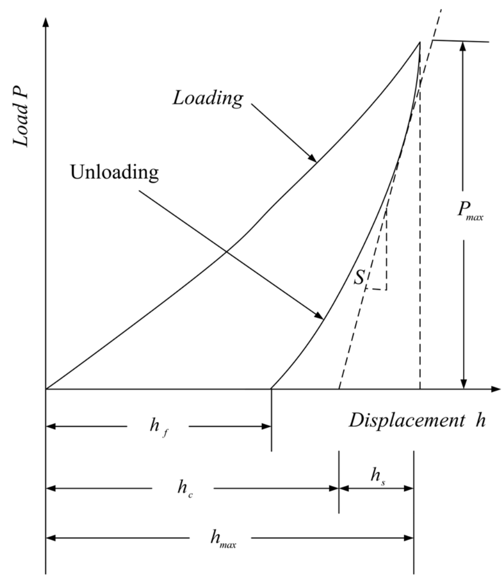


Fig. 1. Schematic representation for load(μN) - depth(nm) data for a nanoindentation experiment.

For an indenter with a known geometry, the projected contact area is a function of the contact depth. The area function for a perfect Berkovich indenter is given by

$$A = f(h_c) = 24.56h_c^2 \tag{5}$$

Indenters used in practical nanoindentation testing are not ideally sharp. Therefore, tip geometry calibration or area function calibration is needed. A series of indentations is made on fused quartz at depths of interest. A plot of A versus h_c can be curve fit according to the following functional form

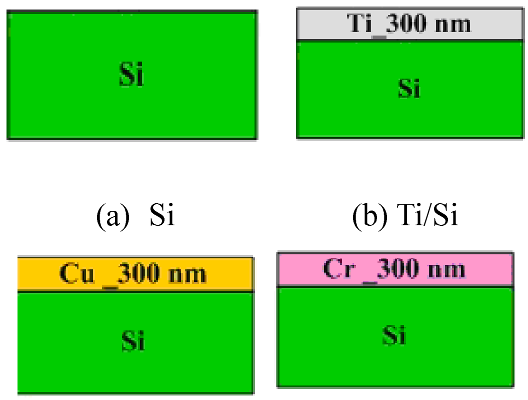
$$A = f(h_c) = 24.56h_c^2 + C_1h_c^1 + C_2h_c^{1/2} + C_3h_c^{1/4} + \ldots + C_8h_c^{1/128} \quad (6)$$

where C_1 through C_8 are constants. The lead term describes a perfect Berkovich indenter.

In this paper, the displacement-load curves were conducted with a high-resolution nanomechanical test. (Fig.1) The $P_{\max}$, $h_{\max}$, h_c, h_f can be determined from displacement-load curves. The Bekervich diamond tip was used E_i = 1140 GPa and ν_i = 0.07. For bulk material Si, the poison ratio ν of bulk material Si were assumed ν_{Si} =0.278 [8] then the elastic modulus of the bulk material Si can be found from equation (1)-(6). Therefore, all the elastic modulus of Ti, Cu, and Cr films on Si substrate (i.e., Ti/Si, Cu/Si and Cr/Si) were obtained by nanoindentation and equation (1)-(6).

3. Numerical simulation

In this investigation, a commercial finite element code ANSYS was used to reproduce the load-depth curves of the bulk material Si and the Ti, Cu and Cr films on Si substrate (i.e., Ti/Si, Cu/Si and Cr/Si) on the nanoindentation process (Fig 2) and the elastic-perfectly plastic material model was considered. An axisymmetric cone with half-included angle of 70.3° which the conical indenter has the same area function as a Berkovich tip was used in this study and the Plan42, Conta171 and Targe169 elements were adopted. As the reported by Lichinchi [8], three-dimensional model was compared with two-dimensional axisymmetric model, no relevant differences are apparent between the two models. Therefore, we have chosen the two-dimensional axisymmetric model in order to restrain the degrees of freedom.



(b) Cu/Si (d) Cr/Si

Fig. 2 Four different type of specimens (a) the bulk material Si (b) the Ti film on Si substrate (c) the Cu film on Si substrate(d) the Cr film on Si substrate

In our work, The bulk material Si and Ti, Cu, and Cr films on Si substrate (i.e., Ti/Si, Cu/Si and Cr/Si) were modeled as the elastic-perfectly plastic materials and all the elastic modulus were obtained by nanoindentation and equation (1)-(6). While the elastic-perfectly plastic material was employed at FEM, the yield stresses ($Y_{Si}, Y_{Ti}, Y_{Cu}, Y_{Cr}$) must be changed for reproducing the load-depth curves.

4. Results and discussion

In this paper, the middle layer effect of multilayered coatings on nanoindentation with Berkovich probe tip was investigated with the finite element analysis. At first, the bulk material Si was studied with a high-resolution nanomechanical test instrument which is a nanoindenter (Triboscope, Hysitron) assembled on an atomic force microscope (Autoprobe, CP-Research), and a three side pyramidal Berkovich probe tip is used in the test. Five indentations were made in each sample at the same maximum loads. Therefore, the nanoindentation testing is successfully and load-depth curve is performed in Fig. 3. As reported by Oliver and Pharr [1], the elasticity modulus and hardness can be determined by their method in nanoindentation but yield stress and other material properties cannot be obtained. The elastic modulus of the bulk material Si introduced in the analysis is determined from Eqs. (1)-(6) as E_{si} =165 GPa . For determining the yield stress and other material properties, the finite element method based on the elastic-perfectly plastic material model is used to reproduce the load-depth curve and the yield stress can be obtain.

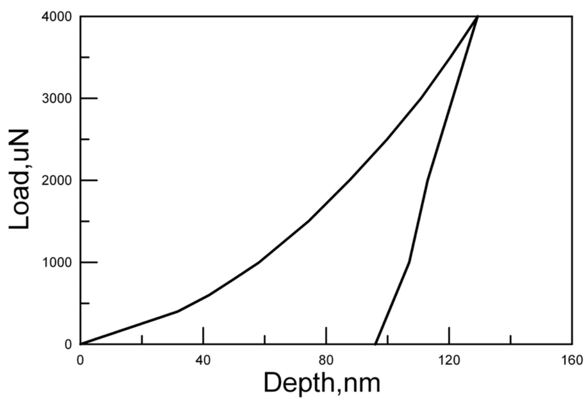


Fig. 3. The load-depth curves of he bulk material Si due to nanoindentation test.

Fig. 4 presents the load-depth curves of the bulk material Si by nanotndentation and FEM in different yield stresses Y_{Si} (5, 6 and 7 GPa), where the linear elastic modulus of Si is E_{Si} =165 GPa. The solid line is the experimental data redrawn from Fig. 4. Comparison of the curves of numerical simulation with experimental curves shows that the loading and unloading curve of simulation by FEM shifts to the right as Y_{Si} ≤ 5 GPa. The smaller yield stress Y_{Si}, the more the curve shifts right. When Y_{Si} = 6GPa the unloading curve of simulation by FEM is very close to the experimental curve. But the loading curve of simulation by FEM shifts to the right and exists the large deviation. This may be due to differences in the actual and assumed yield stress or due to the use of a constitutive model of materials like elastic perfectly-plastic one without work-hardening rate or due to the rounding of the tip as a result of wear.

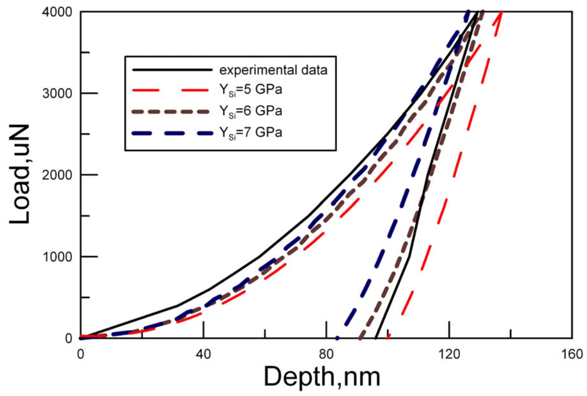
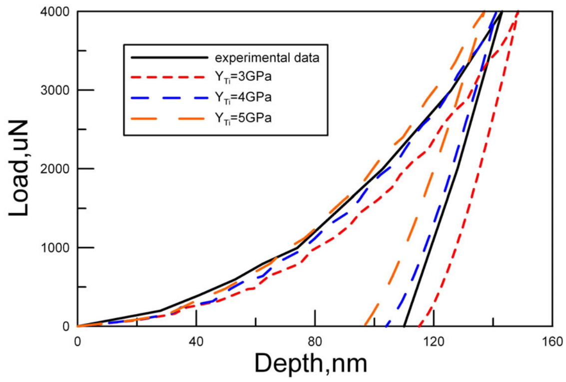
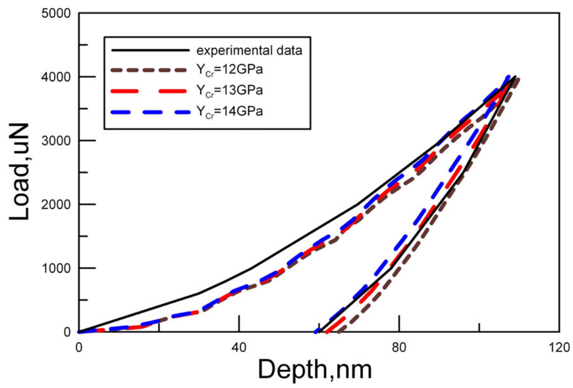


Fig. 4. The load-depth curves of he bulk material Si by nanotndentation and FEM in different yield stress Y_{Si}.

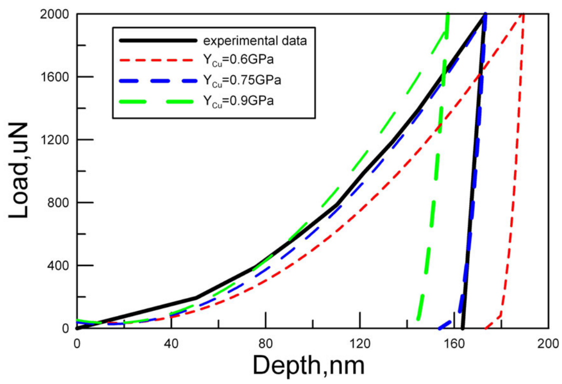
For single layer films, the 300nm thickness of Ti, Cr and Cu films on Si substrate (i.e., Ti/Si, Cu/Si and Cr/Si) (Fig. 2) were conducted with a high-resolution nanomechanical test. The Young's modulus of the Ti, Cr and Cu films can be obtained by using the Oliver and Pharr method (Eqs. (1)-(6)) as E_{Ti} =134GPa, E_{Cr} =240GPa, and E_{Cu}=110GPa. Inquiring further into the yield stress of all films, Fig. 5 shows the load-depth curves of the Ti, Cr and Cu films on Si substrate (i.e., Ti/Si, Cu/Si and Cr/Si) by nanotndentation and FEM in different yield stresses, Comparison of the curves of numerical simulation with experimental curves shows that the yield stress of Ti, Cr and Cu films can be obtain as Y_{Ti}=4Gpa,. Y_{Cr}=13GPa, and Y_{Cu}=0.75GPa.



(a) Ti/Si (E_{Ti} =134GPa, E_{Si} =165GPa)



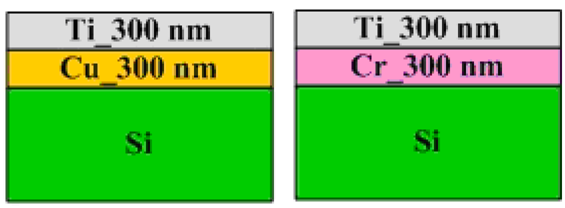
(b) Cr/Si(E_{Cr} =240GPa, E_{Si} =165GPa)



(c) Cu/Si(E_{Cu} =110GPa, E_{Si} =165GPa)

Fig. 5. The load-depth curves of 300nm thickness single layer films Ti/Si, Cr/Si, and Cu/Si by nanotndentation and FEM in different yield stress(Y_{Ti} ,. Y_{Cr} , and Y_{Cu})

In addition, multilayered coatings with 300nm thickness and different material (i.e., Ti/Cu/Si and Ti/Cr/Si) of the middle layer (Fig. 6) were conducted by nanoindentation and simulated by finite element analysis in Fig 7, and all the Young's modulus and yield stress of material are mention above. Comparison of the curves of numerical simulation with experimental curves shows that the loading and unloading curve of multilayered coatings Ti/Cu/Si simulation by FEM shifts to the left, and the loading and unloading curve of multilayered coatings Ti/Cr/Si simulation by FEM shifts to the right but all are very close to the experimental curve. This may be due to the errors of every single layers described before or for a variety of factors at coating process. Furthermore, it is concluded that the finite element approach is capable of reproducing the load-depth curves of nanoindentation test at multilayered coatings problems.

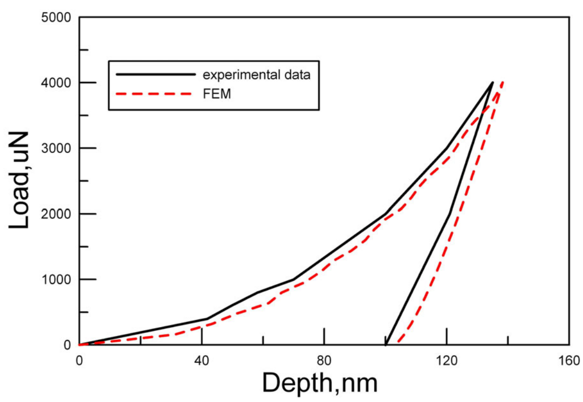


(a) (b)

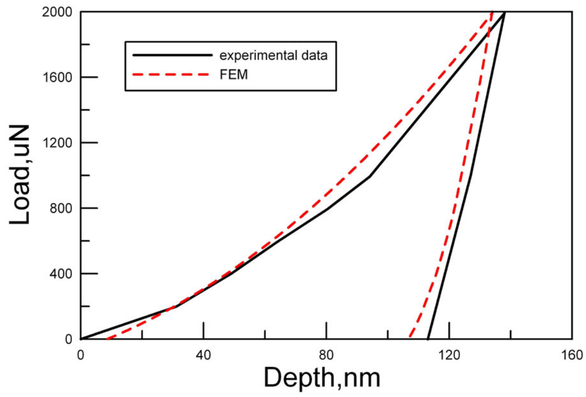
Fig. 6. multilayered coatings with 300nm thickness and different material of the middle layer (a) Ti/Cu/Si and (b) Ti/Cr/Si

Finally, we are further to analyze the effect of middle layer, Fig. 8 presents the load-depth curves of single layer Ti/Si and multilayered coatings Ti/Cu/Si and Ti/Cr/Si with 300nm thickness every layer by nanotndentation and FEM. Comparison of the curve of multilayered coatings Ti/Cu/Si with the curve of single layer Ti/Si shows that the loading and unloading curve shifts to the right, but the curve of multilayered coatings Ti/Cr/Si with the curve of single layer Ti/Si shows that the loading and unloading curve shifts to the left. It is concluded that the harder middle layer material is the harder surface film response.

Fig. 10 presents the load-depth curves of multilayered coating Ti/Cu/Si by FEM in difference thickness of middle layer Cu (100nm, 300nm, 500nm and 1000nm)(Fig. 9). It shows the loading and unloading curve shifts to the right while getting larger thickness of middle layer Cu. Because the material of middle layer Cu is softer than the surface film Ti, it is concluded that the lager thickness of soft middle layer material is the softer surface film response.



(a) Ti/Cr/Si



(b) Ti/Cu/Si

Fig. 7. The load-depth curves of multilayered coatings with 300nm thickness every layer by nanotndentation and FEM in different middle layer Cu or Cr (i.e., Ti/Cu/Si and Ti/Cr/Si).

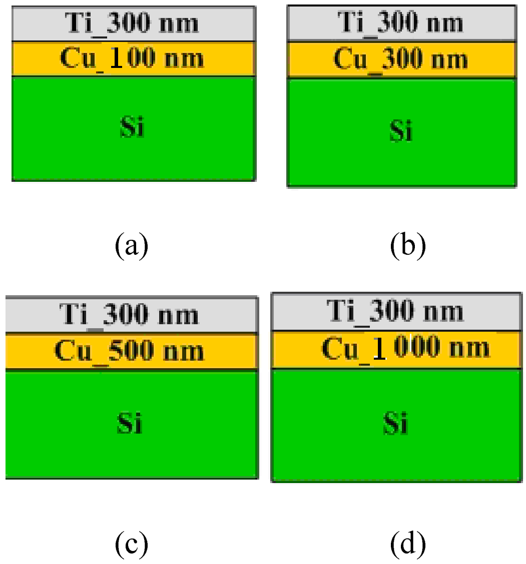


Fig. 9. The multilayered coating Ti/Cu/Si in difference thickness of middle layer Cu (a)100nm (b) 300nm (c) 500nm (d) 1000nm.

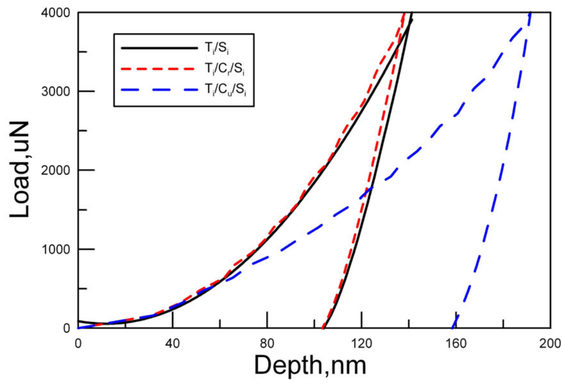


Fig. 8. The load-depth curves of single layer Ti/Si and multilayered coatings Ti/Cu/Si and Ti/Cr/Si with 300nm thickness every layer by nanotndentation and FEM.

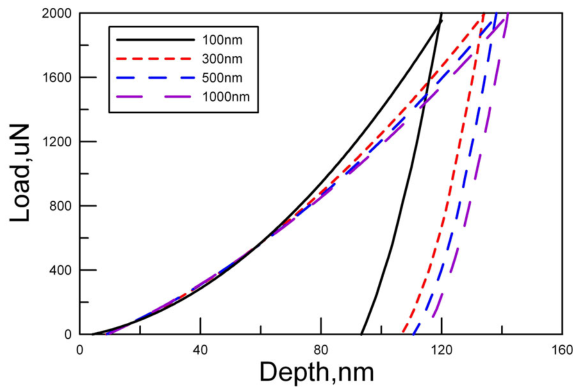


Fig. 10. The load-depth curves of multilayered coatings Ti/Cu/Si by FEM in difference thickness middle layer Cu.

5. Conclusions

FEM simulation with the commercial software ANSYS provided important observations of the middle layer effect of multilayered coatings on nanoindentation with Berkovich probe tip was investigated. The numerical results are compared with the experimental data, and the following conclusions are obtained.

1. Comparison between the experimental data and numerical results demonstrated that the finite element approach is capable of reproducing the load-depth curves of nanoindentation test at multilayered coatings problems.
2. Comparison of the curve of multilayered coatings Ti/Cu/Si with the curve of single layer Ti/Si shows that the loading and unloading curve shifts to the right, but the curve of multilayered coatings Ti/Cr/Si with the curve of single layer Ti/Si shows that the loading and unloading curve shifts to the left. It is concluded that the harder middle layer material is the harder surface film response.
3. When the load-depth curves of multilayered coating Ti/Cu/Si by FEM in difference thickness of middle layer. It shows the loading and unloading curve shifts to the right while getting larger thickness of middle layer. Because the material of middle layer Cu is softer than the surface film Ti, it is concluded that the lager thickness of soft middle layer material is the softer surface film response.

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