STUDY OF MECHANICAL PROPERTIES OF NANOSTRUCTURED POLYMER COATINGS PREPARED USING PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

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Abstract

The aim of the present work was to deposit transparent polymer $SiO_xC_yH_z$ protective coatings from hexamethyldisiloxane/oxygen mixtures in capacitively coupled glow discharge. The coatings prepared under dusty plasma conditions showed nanocomposite character. Complex characterization of the local mechanical properties was carried out on the prepared samples from nano to microscale using indentation techniques. The coatings were very elastic, they exhibited high elastic recovery and low plastic deformation even at indentation depths approaching the coating thickness.

Keywords: PECVD, hexamethyldisiloxane, mechanical properties, nanoDMA

1. INTRODUCTION

The aim of the present work is to develop a method for transparent protective coating deposition on the surfaces of plastics such as polycarbonates, having a high level of abrasion resistance and improved resistance against cracking under exposure to thermal and mechanical stresses. Among the various techniques used for preparation of transparent scratch-resistant coatings the plasma chemical methods have received a great deal of attention by researchers and have been extensively reported in the literature [1-8]. Plasma chemical methods are generally using a mixture of hard-coating precursors (e.g. organosililicon or organosilazane mixtures with oxygen in the case of transparent coatings) in a high-frequency or corona discharges. The product is deposited directly on a plastic substrate in form of a very thin film. The physical and chemical properties of the resulting films depend strongly on the process parameters, such the frequency, coupling type, applied power, bias voltage, precursor type, the power per unit monomer mass flow, and whether or not an oxidant is added. Thus using the plasma chemical vapor deposition (PECVD) method, thin films with a wide range of mechanical properties can be produced from hard inorganic SiO_2-like to soft polymer-like $SiO_xC_yH_z$ films properties just varying the plasma conditions. Moreover, under specific conditions films with special structures, such nanocomposite SiOCH or nanocomposite SiO_2-containing diamond-like carbon films may be prepared.

The main objective of the present work was to deposit protective films in capacitively coupled radiofrequency discharges from hexamethyldisiloxane ($C_6H_{18}Si_2O$ - HMDSO) oxygen mixtures. These types of films are of particular interest in various applications because they exhibit a number of desirable properties: good adherence to polymer substrates, rate, good transparency to visible radiation, good thermomechanical stability etc. relatively high deposition

2. EXPERIMENTAL

The studied films were deposited by PECVD from a mixture of HMDSO ($C_6H_{18}Si_2O$) and oxygen. The ratio of HMDSO flow rate Q_{HMDSO} and the total flow rate q ($q=Q_{HMDSO}/(Q_{HMDSO}+ Q_{O2})$) ranged from 0 to 0.95. The HMDSO flow rate Q_{HMDSO} varied from 0 to 20 sccm, the oxygen flow rate Q_{O2} was varied from 3 to 11 sccm. The substrates were silicon wafers a polycarbonate plates. The capacitively coupled plasma was generated in a parallel plate reactor using an r.f. generator working at frequency of 13.56 MHz. The applied power P varied from 50 to 150 W and the negative bias voltage ranged from -10 to -300 V.

The elemental composition, thickness and density, were determined using nuclear analytical methods, RBS (Rutherford backscattering spectrometry) and ERDA (elastic recoil detection analyses). The conventional ERDA with 2.5MeV alpha projectiles was used for hydrogen estimation. For a detailed analysis of recorded experimental spectra the codes GISA 3 and SIMNRA 6.06 were used [9-11].

The instrumented indentation technique was used to study the mechanical properties of the films. The samples were measured by means of Fischerscope H100XYp microindentor. The selected samples were measured on Hysitron TI 950 nanoindentor. The modulus mapping capability was applied to obtain quantitative maps of the storage and loss stiffness and the storage and loss modulus. The modulus mapping combines the in-situ imaging capabilities with the ability to perform nanodynamic mechanical analysis. During the imaging process, the system continuously monitors the dynamic response of the sample to the oscillating load as a function of the position. Therefore, at each image pixel (typically 256×256 pixels), the storage and loss moduli are found if the geometry of the indenter is known. At the same time, one can also gain information about the sample surface morphology. The morphology of the film surface and the indentation prints were studied by MIRA 3 scanning electron microscope made by Tescan and by atomic force microscope Ntegra Prima NT-MDT.

Table 1 Summary of the deposition conditions for selected samples. Q_{O2} is the oxygen flow rate, Q_{HMDSO} is the HMDSO flow rate, P is the applied power, U_b is the corresponding negative bias voltage, p is the deposition pressure. The deposition time was 60 minutes

Sample	Q_{O2} [sccm]	Q_{HMDSO}[sccm]	P [W]	U_b [V]	p [Pa]
VI43	6.3	0.5	50	-49	41
VI47	5.0	2.4	50	-107	27
VI60	6.0	1.2	50	-134	27
VI61	8.2	0.7	50	-138	32
VI65	11.0	3.5	50	-36	44
VI68	6.9	3.1	75	-177	33
VI72	6.7	0.6	75	-203	30
VI75	3.9	2.3	75	-140	25
VI77	3,6	3,0	25	-20	22

3. RESULTS AND DISCUSSION

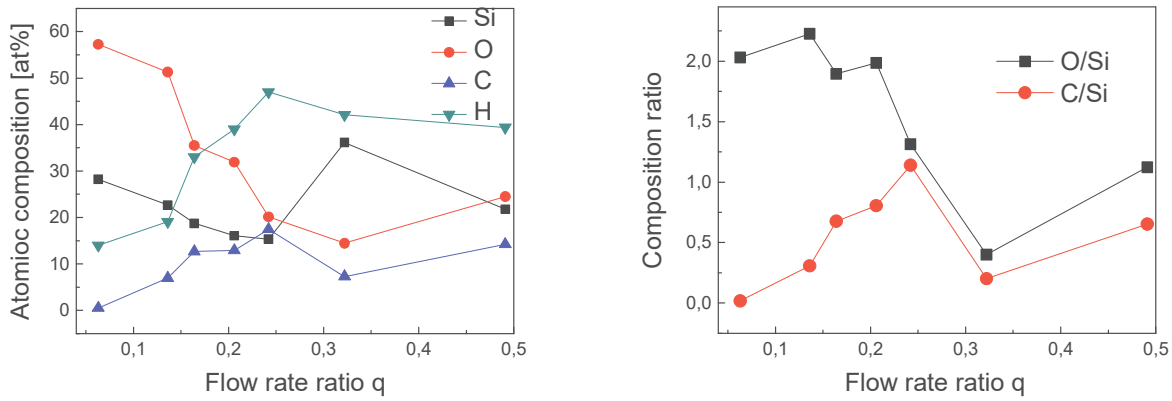

Fig. 1 The dependence of the atomic composition on the flow rate ratio q (on the left) and the dependence of oxygen and carbon to silicon ratios on the flow rate ratio q (on the right)

A large number of depositions were carried out in a wide range of deposition conditions in order to find the deposition process parameters for preparation of coatings with optimum hardness, elastic modulus, fracture toughness and good adhesion to polycarbonate substrates. In **Table 1** the summary of characteristic deposition parameters are listed for selected samples. In **Fig. 1** the composition and the oxygen and carbon

to silicon ratio dependences on the HMDSO-to-oxygen flow rate ratio q (q=QHMDSO/(QHMDSO+ QO2)) obtained by means of combined RBS/ERD analysis are illustrated.

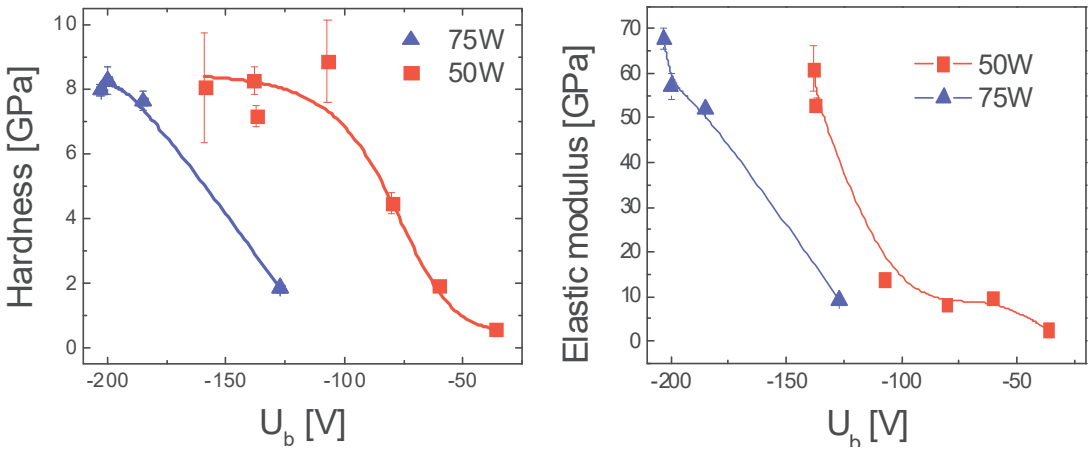

Fig. 2 The dependence of the hardness (on the left) and the elastic modulus on the bias voltage (on the right) for to applied powers 50 and 75 W

The deposition conditions suitable for nanocomposite film preparation were achieved due to a relatively high HMDSO to oxygen flow rate ratio, which led to the creation of dusty plasma because of the relatively low applied power [9]. The composite character of the produced film improved its mechanical stability. Examples of the nanocomposite structure are shown in **Fig. 3** and **Fig. 4**.

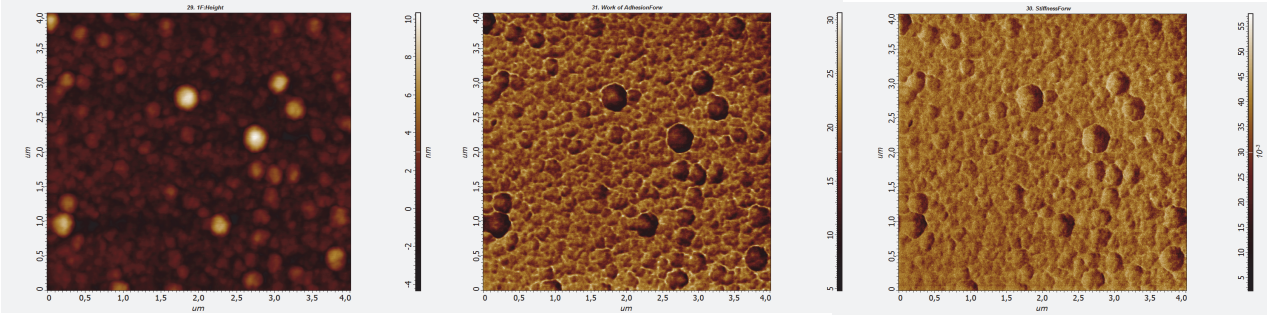

Fig. 3 Example of topography image (on the left) obtained using AFM imaging of nanocomposite film, map of the work of adhesion in mJ/m^2 (in the middle) and the stiffness map in N/m (on the right)

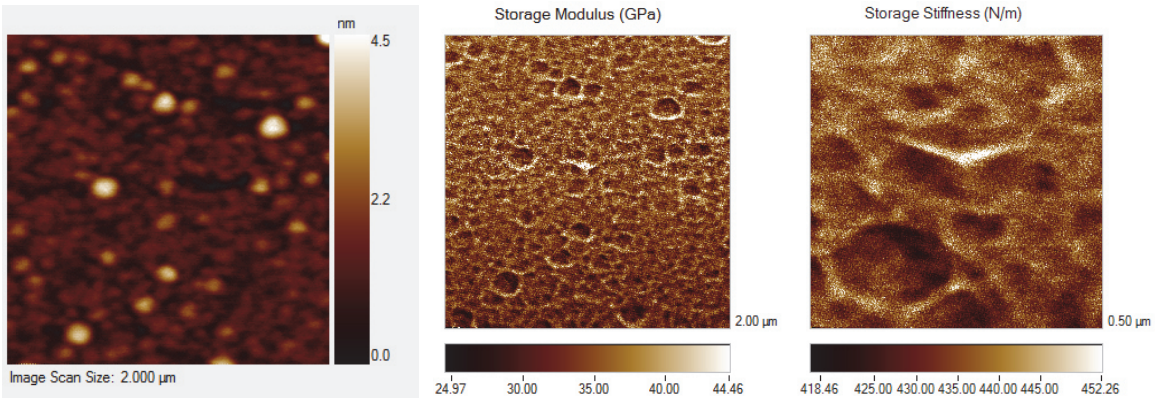

Fig. 4 Example of 2x2 µm^2 topography image (on the left) of nanocomposite film [RMS (root mean square roughness) = 0.9 nm, Ra (average roughness) = 0.6 nm], storage modulus map on the same area (in the middle) and detail of storage stiffness map (on the right) on area of 500x500 nm^2

Fig. 4 shows the modulus mapping results carried out on nanocomposite film. The maps were obtained using a diamond Berkovich indentor with a scanning rate of 0.2 Hz, oscillation frequency of 200 Hz, contact force of 4 μN, oscillation amplitude of 2 μN, and displacement amplitude around 1 nm.

The local mechanical maps in **Fig. 4** show that the storage modulus as well as storage stiffness of the amorphous matrix is higher than that of the amorphous siloxane particles. The loss modulus and loss stiffness values for both particles and matrix were negligible. That agrees with the quasistatic nanoindentation results, where the elastic and viscoelastic response of the coating was dominating. In **Fig. 5** the results of microindentation tests carried out for several indentation depths on coatings deposited on two different substrates, single crystalline silicon and polycarbonate, are compared. The indentation loads ranged from 10 to 100 mN.

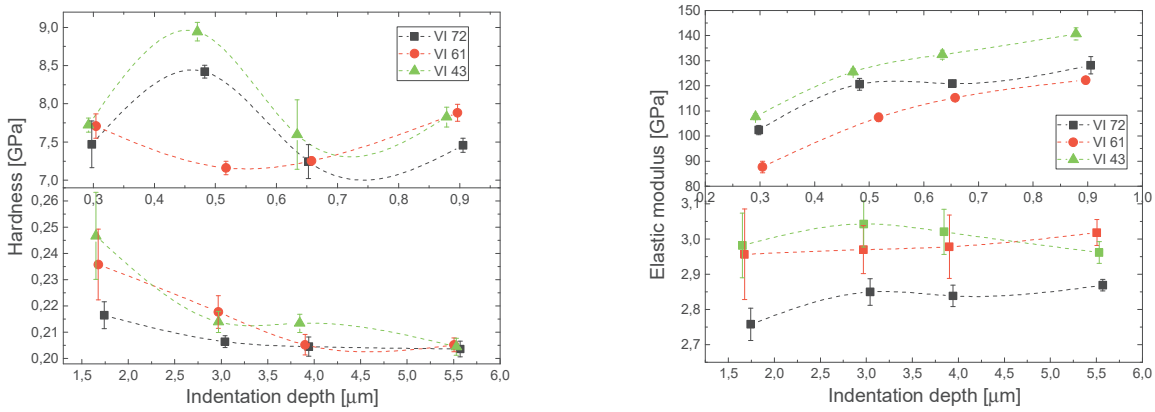

Fig. 5 (on the left) Examples of the hardness dependences on the maximum indentation depth for films deposited on silicon substrates (top) and on polycarbonate substrates (bottom). (on the right) The dependence of elastic modulus on the maximal indentation depth for coatings on substrates (top) and on polycarbonate substrates (bottom). The dashed lines are only guides for eyes. The coatings deposition conditions are given in the **Table 1**.

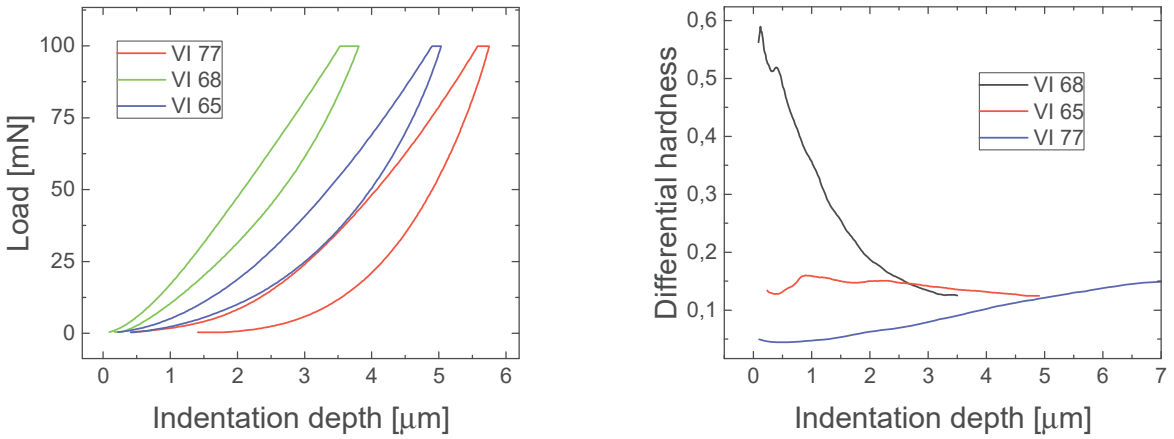

Fig. 6 (on the left) Examples of loading/unloading curves for coatings deposited on polycarbonate samples. (on the right) Examples of differential hardness (in GPa) dependence for coatings on polycarbonate samples. The differential hardness was calculated as the derivative of the load function with respect to the increasing contact area. The deposition conditions of the selected coating are given in **Table 1**.

The nanocomposite samples were able to withstand indentations with relatively large loads and indentation depths approaching half of the film thickness without significant plastic deformation. Moreover, the film showed high extent of anelastic (viscoelastic) recovery. This is illustrated in **Fig. 6**, which shows the loading/unloading curves obtained on nanocomposite coatings deposited on polycarbonate. Although the maximum indentation

depth approaches the film thickness, the irreversible indentation work is very low compared to the elastic reversible indentation work. Moreover, there was in each case a significant anelastic recovery, thus the indentation prints faded away after a short time.

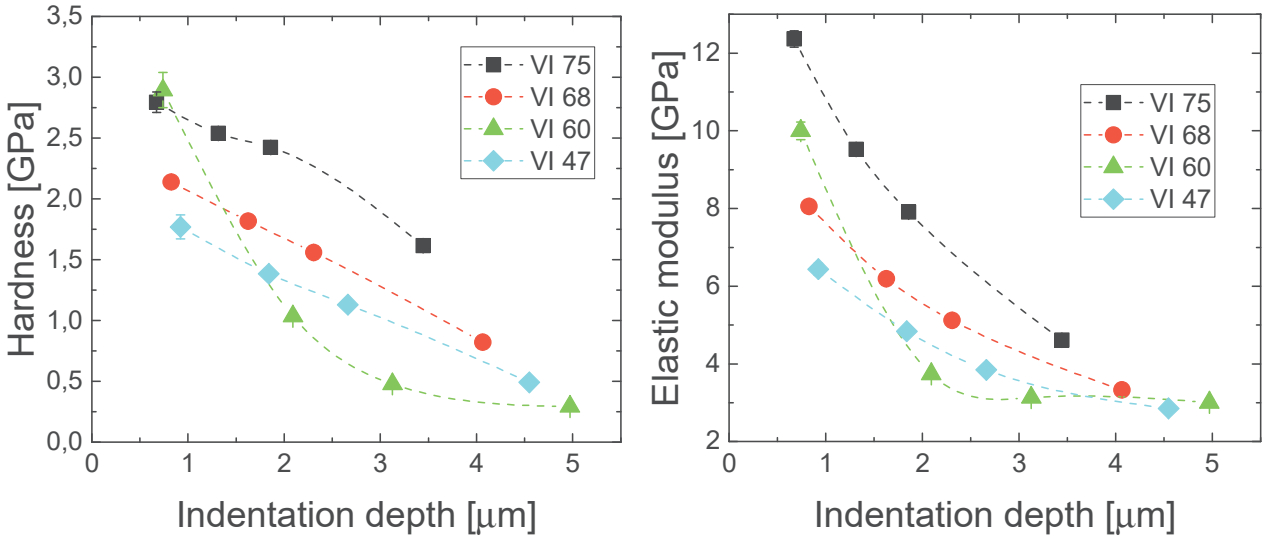

Fig. 7 (on the left) The dependence of the hardness on the indentation depth for coatings on polycarbonate substrates. (on the right) The dependence of elastic modulus on the indentation depth for coatings on polycarbonate samples. The deposition conditions of the selected coating are given in **Table 1**.

Fig. 7 shows the dependences of the measured hardness and elastic modulus on the indentation depth for coatings deposited on polycarbonates. Because the hardness and elastic modulus of the films are an order of magnitude higher than that of the substrate, it is difficult to find enough low indentation load to measure the film material parameters directly. Therefore the apparent (or composite) material parameters were measured at several indentation depths to study the effect of the substrate on the measured values. From the obtained dependence of apparent material parameters on the indentation depth it was possible to estimate the film parameters. Moreover, the tests at larger indentation depths gave information about the crack and delamination resistance of the prepared coatings. The coatings presented in **Fig. 7** were able to withstand the indentation without cracking or delamination even when the indentation depth approached the film thickness.

4. CONCLUSION

Thin films with a wide range of mechanical properties were produced from hard inorganic (SiO_2 like) to soft polymer-like ($SiO_xC_yH_z$ films) properties just by varying plasma conditions. The sample set contained hard (SiO_2 like) films with hardness reaching 9 GPa and elastic modulus reaching 70 GPa, as well as soft $SiO_xC_yH_z$ films with hardness around 0.2 GPa and elastic modulus around 3 GPa. The organosilicon plasma polymer films prepared under optimum conditions exhibit several desirable properties: good adherence to polymer substrates, a relatively high deposition rate, good transparency to visible radiation, good thermomechanical stability, high elasticity and excellent fracture toughness. Some of the films were grown under dusty plasma conditions. These films showed nanocomposite character, which improved the film's mechanical stability; however, the particles embedded in the amorphous $SiO_xC_yH_z$ matrix also increased the film's roughness. On the other hand, high roughness and low surface free energy improved the hydrophobic character of the film's surface. The nanocomposite films exhibited high elasticity, they were able to withstand indentation tests with depths approaching the film thickness with negligible plastic deformation on both single silicon and polycarbonate substrates, without cracking or delamination.

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REFERENCES

[1] BOUSQUET A., BURSIKOVA V., GOULLET A., DJOUADI A., ZAJICKOVA L., GRANIER A., Comparative Study of Films Deposited from HMDSO/O(2) in Continuous Wave and Pulsed rf Discharges, Surface & coatings technology, Vol. 200, 2006, pp. S287-S293.

[2] SEPEUR S., KUNZE N., WERNER B., ET. AL. AND SCHMIDT H., UV curable hard coatings on plastics, Thin Solid Films Vol. 351, 1999, pp. 216-219.

[3] ZAJÍČKOVÁ L., BURŠÍKOVÁ, V., JANČA J. Protection coatings for polycarbonates based on PECVD from organosilicon feeds, Vacuum, Vol. 50, No. 1-2, 1998, pp. 19-21.

[4] MOCANU V., STOICA A., KELAR L., FRANTA D., BURŠÍKOVÁ V., MIKŠOVÁ R., AND PEŘINA V., Multifunctional transparent coatings on polycarbonates prepared using PECVD, Chem. Listy, Vol. 106, 2012, pp. s1460.

[5] RATS D., HAJEK V., MARTINU L., Micro-scratch analysis and mechanical properties of plasma-deposited silicon-based coatings on polymer substratesThin Solid Films, Vol. 340, 1999, 33-39.

[6] MARTINU L., Plasma Processing of Polymers, 1997, edited by R.d'Agostino et.al. (Kluwer Academic Publisher), pp. 247.

[7] ZAJÍČKOVÁ L., BURŠÍKOVÁ V., PEŘINA V., MACKOVÁ A., SUBEDI D.P., JANČA J., SMIRNOV S., Study of argon plasma treatment of polycarbonate substrate and its effect on film deposition Surface & coatings technology, Vol. 142-144, 2001, pp. 489-504.

[8] SOBRINHO A.S.S., SCHÜHLER E., KLEMBERG-SAPIEHA J.E., WERTHEIMER M.R., ANDREWS M. AND GUJRATHI S.C., Plasma-deposited silicon oxide and silicon nitride films on poly(ethylene terephthalate): A multitechnique study of the interphase regions J. Vac. Sci. Technol. A. Vo. 16 No. 4, 1998, pp. 2021-2030.

[9] CAMPBELL, A.C., KLAPETEK, P.,VALTR M., BURŠÍKOVÁ V., Development of reference materials for the investigation of local mechanical properties at the nanoscale, Surface and Interface Analysis, Vol. 44 No. 8, 2012, pp. 1151-1154.