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Some thermodynamic effects in thin film adhesion

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The following thermodynamic effects have been studied in experiment: the normal adhesion of Ge films as a function of the surface energy of substrate (glass, mica, Al, Cu); the normal adhesion of Ge, Al, Cu and Cr films to Cu and (001) NaCl substrates as a function of the specific surface energy of the film; the dimensional dependence of Cu and Cr adhesion within thickness range of 20 to 250 nm; effect of finely dispersed ferromagnetic and weakly magnetic powders used as fillers in partially crystallized polymer substrates with relatively low specific surface energy on Al film adhesion. An increase in the film thickness as well as in the specific surface energy of the substrate and the film has been found to result in weakened adhesion.

Экспериментально изучены следующие термодинамические эффекты: зависимость нормальной адгезии пленок Ge от удельной поверхностной энергии подложки (стекло, слюда, Al, Cu); зависимость нормальной адгезии от удельной поверхностной энергии пленки (Ge, Al, Cu и Cr) на подложках Cu и (001) NaCl; размерная зависимость адгезии пленок Cu и Cr в интервале толщин 20–250 нм; влияние наполнения частично-кристаллических полимерных подложек с относительно малой удельной поверхностной энергией мелкодисперсными ферро- и слабомагнитными порошками на адгезию пленок Al. Установлено, что увеличение толщины пленки, удельной поверхностной энергии подложки или пленки приводит к уменьшению адгезии.

The problem of film material adhesion draws continuously the attention of both theorists [1] and experimenters (see e.g. [2, 3]). Basing on the known fact that the adhesion of two materials is a result of molecular interaction, ionic or metallic binding, authors [1] have studied adhesion properties of two metals separated by a dielectric layer, of a metal (Me)/dielectric (D) system containing a vacuum gap as well as of a Me/vacuum/D/vacuum/Me system. To that study, the electron density functional method was used. In [1], the electron density distribution has been determined, the interphase energy (σ_{sf} where indices s and f refer to substrate and film, respectively), the adhesion free energy (σ_A), and adhesive interaction energy (F_A) have been calculated, and limiting cases where the vacuum or dielectric layer thickness tends to zero have been considered. Note that it is just the limiting causes that are of the highest interest, since those correspond to experimental conditions.

Our purpose, besides of qualitative comparison of the results obtained with the conclusions of [1], consists in the study of the film thickness and the specific surface energy of the film (σ_f) or substrate (σ_s) material influence on the normal (A_n) and sometimes tangential (A_τ) adhesion. The effect of σ_f and σ_s can be drawn directly from the expression for the work of the adhered film tear-off:

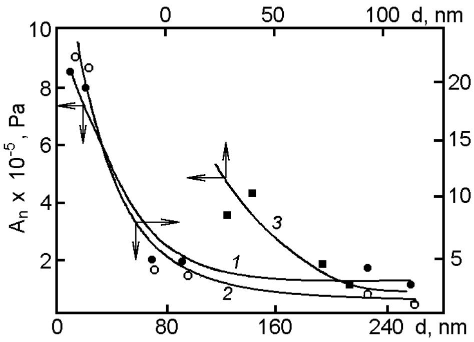

Fig. 1. A_n and A_τ dependence on the Cu (*1*, *2*) and Cr (*3*) film thickness on glass substrates at 300 K.

$$W_A = -\sigma_A = \sigma_{sf} - \sigma_s - \sigma_f. \quad (1)$$

Since the surface energy σ_f is a function of thickness [4], then, taking (1) into account, the thermodynamic effects of adhesion can be considered as functions of σ_f, σ_s, σ_{sf} and d. The set of those questions is not still scarcely studied to date, and that is predefined our study task.

The adhesion measurement method was based on the Strong technique, wherein the tear-off force of a sticky tape with the film from the substrate and the contact area (S) are measured and the quantity $A = F_A/S$ is found. The tangential adhesion is determined by extrapolating the angle φ between the force action direction and the substrate plane to zero, while at $\varphi = 90°$, the normal adhesion is. In this case, the fixation of the film tear-off moment is a considerable difficulty. To that end, we used a laboratory unit (described in [4] in detail) provided with an electron displacement sensor that allows to fix the film tear-off moment at high precision. As the electron sensor, a transformer sensor of solenoid type is used basing on the dependence of a coil inductance on the position of a ferrite core therein. The core, in turn, is connected with a spring device coupled with a micro-screw setting the tear-off force; the other end of the spring is connected with the tape holder. To measure the force F_A at different angles φ, the object table rotation through fixed angles has been provided.

The film samples were obtained in a standard vacuum unit VUP-5M (residual pressure of about 10^{-3} Pa) by resistive evaporation and deposition of Ge, Al, Cu, and Cr films onto glass, mica, C, Al, Cu, Cr, and (001) NaCl substrates or by magnetron sputtering of Al films onto substrates made

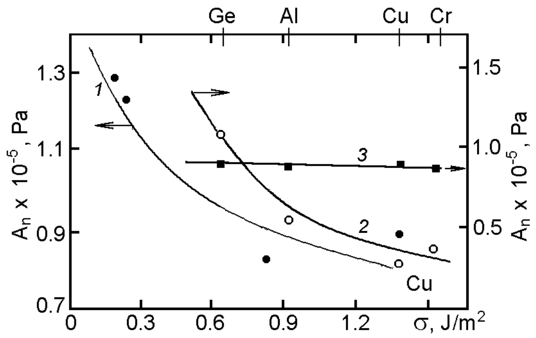

Fig. 2. A_n dependence on the substrate surface energy for 65 nm Ge film (*1*) and on the film material surface energy (for Ge, Al, Cu, and Cr films) on dielectric substrate (001) NaCl (*2*) and on metal (Cu) substrate (*3*). The Ge, Al, Cu, and Cr films are 60 to 80 nm thick.

of partially crystalline polymer materials (polyethylene, polycaproamide, pentaplast, poly-4-methylpentene-1 (P4MP1) containing finely dispersed ferromagnetic and weakly-magnetic powders (Fe, Ti, quartz, barium ferrite, and graphite) as fillers. In some cases, the samples from the latter series were annealed at 350 to 470 K.

The dimensional dependence of A_n and A_τ was studied taking Cu and Cr films as examples (see Fig. 1). It is seen from these data that A_τ exceeds A_n by several times. This can be explained by the action of tangential friction forces resulting from the phase interaction at the film/substrate interface.

Thus, we can write $A_\tau = A_n + \Delta A_{sf}$ where the additive ΔA_{sf} is due to energy σ_{sf}. It is to note that the quantity ΔA_{sf} plays a considerable part in tensosensitivity phenomenon (see, e.g., [5]), since the longitudinal straining force cannot exceed the filn tear-off force in tangential direction. The adhesion dependence on the film thickness can be substantiated in the frame of concept [1] concerning the adhesion forces in the Me/D system. In contact, the double electrical layer of the metal causes the dielectric polarization, thus resulting in repulsion of positively charged surfaces. The polarization extent increases obviously as the thickness rises, thus causing a monotonous weakening of the adhesion.

Fig. 2 presents thermodynamic effects associated with the film or substrate surface energy. The A_n dependence on σ_s follows qualitatively from the Eq.(1). Distinctions between the dependences 2 and 3 are explainable by the conclusions presented in [1]. According thereto, the repulsive forces

Table. Normal adhesion of Al films on various polymer substrates

Substrate	T_{anneal}, K	$A_n \cdot 10^{-5}$, Pa	Substrate	T_{anneal}, K	$A_n \cdot 10^{-5}$, Pa
Polyethylene	300	14.3	Pentaplast + barium ferrite (25 % by mass)	300	9.5
	350	15.8			
Polycaproamide	300	10.0	P4MP1 + graphite (25 % by mass)	300	10.5
	470	19.0			
Pentaplast	300	9.8	P4MP1 + iron (25 % by mass)	300	3.9
	430	18.0			
Pentaplast + graphite (25 % by mass)	300	1.1	P4MP1 + quartz (25 % by mass)	300	8.8
Pentaplast + iron (25 % by mass)	300	2.5	P4MP1 + titanium (25 % by mass)	300	5.8
Pentaplast + quartz (25 % by mass)	300	3.1	P4MP1 + barium ferrite (25 % by mass)	300	6.2
Pentaplast + titanium (25 % by mass)	300	3.4			

arise in the Me/D system while in the Me/Me one, only attraction forces act in the case when there is no gap at the interface.

In Table, presented are the study results on normal adhesion of Al thin films ($d \cong$ 80 nm) on various substrates made of partially crystalline polymers with and without fillers. Since thermally deposited Al films show a very low adhesion, the magnetron sputtering was used in this experimental series. A specific feature of the polymer substrate preparation consisted in that the powder mixture of the polymer with filler was held for several minutes at a temperature exceeding the polymer melting one by 10 to 20 K and then crystallized in a rotating magnetic field generated using a device made from a 3-phase motor stator. Such substrates have layered structure independent of the filler type.

The data of Table allow to suppose the following adhesion features of Al films. Annealing of the film/substrate system results in an increased adhesion that can be explained by a partial relaxation of macroscale stresses in the substrate and possible diffusion processes. Addition of a filler into pentaplast causes an appreciable adhesion weakening (except for Ba ferrite filler) that may be associated with change in the substrate dielectric constant (according to [1], the adhesion is lowered as the constant increases), with the polymer layer thickness separating the Al film from the ordered filler particular layer as well as with other factors being difficult to control. The correlation absence between A_n values for pentaplast and P4MP1 substrates containing the same fillers indicates the necessity of further studies directed to establishing of correlation between the adhesion strength and the layered substrate stcurtures. The fact that the film adhesion on polymer substrates is much weaker than in the case of bulk samples requires also a special study.

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Деякі термодинамічні ефекти у адгезії тонких плівок

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Експериментально вивчено такі термодинамічні ефекти: залежність нормальної адгезії плівок Ge від питомої поверхневої енергії підкладки (скло, слюда, Al, Cu); залежність нормальної адгезії від питомої поверхневої енергії плівки (Ge, Al, Cu і Cr) на підкладках Cu і (001) NaCl; розмірна залежність адгезії плівок Cu і Cr в інтервалі товщин 20–250 нм; вплив наповнення частково-кристалічних полімерних підкладок з відносно малою поверхневою енергією мілкодисперсними феро- та слабкомагнітними порошками на адгезію плівок Al. Встановлено, що збільшення товщини плівки, питомої поверхневої енергії підкладки або плівки призводить до зменшення адгезії.