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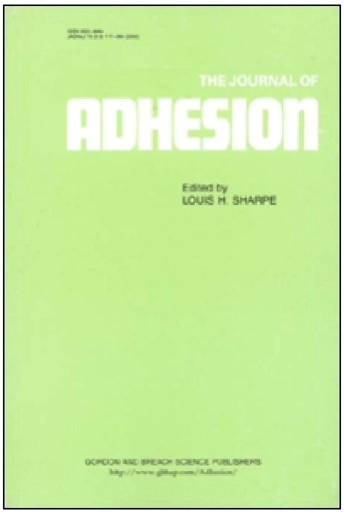

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Light-Modulated Electrostatic Double Layer Adhesion

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Light-Modulated Electrostatic Double Layer Adhesion

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Centrifuge measurements have been carried out which show a significant contribution of the electrostatic double layer to adhesion between solids. By variation of the illumination of the adhesive system, Zr-coated gold spheres on CdS single-crystals, the electronic properties of the photoconducting CdS and hence the electrostatic double layer force at the interface are varied whereas other forces (van der Waals, H_2O layer) remain unaffected. Qualitatively, the experimental results are in agreement with a simple model of the metal-semiconductor contact. Either surface contaminants or surface asperities would prevent quantitative agreement with this theory.

INTRODUCTION

The importance of van der Waals and other types of forces in particle adhesion is well established.[1] Yet, there is insufficient quantitative evidence on the contribution of electrostatic double layer forces. This paper describes an experimental method by which the two forces can be measured separately.

The principal ideas on electrostatic double layer forces have been described in detail elsewhere:[1,2] Solids of different work functions form an electrostatic double layer at their common interface. The resulting potential drop acts as in a simple capacitor arrangement, the two solids attract each other.

In the case of metallic adherents, the calculation of electrostatic double layer attraction is comparatively simple and involves only geometry. If one of the adherents, however, is a semiconductor or an insulator, it is more difficult because the charges separated at the interface can accumulate in surface states and in the space charge below the surface.

A further problem is the fact that the electrostatic double layer forces depend on surface properties—work function, surface state density—which are very sensitive to contaminants.

This paper describes a method which permits direct measurement of electrostatic double layer forces in an adhesive system consisting of metal spheres placed on a photoconducting substrate[3] whose electronic properties can be varied by illumination. Illumination of a metal-photo-conductor interface changes only the electronic properties and thus the electrostatic double layer adhesion, whereas the van der Waals component and other types of adhesion forces remain unaffected. We will rule out photo-desorption in a concluding experiment.

The present report describes measurements of this kind using photoconductive CdS single crystal platelets and Zr-coated gold spheres.

ADHESIVE SYSTEM

The $(11\bar{2}0)$-surface of highly photo-conductive CdS crystals[4] grown in the vapor phase were used as substrates. The other adherents were Zr-coated Au spheres (diameter 3 to 5 μm). The Zr was evaporated onto Au spheres in a moderate vacuum. The Zr layer thickness was 0.05 to 0.5 μm. The Au spheres were prepared by droppng a high purity gold powder (Doduco KG, Pforzheim, Germany) through a vertical tube furnace, whose maximum temperature in the middle of the tube was about 1200°C. The irregularly shaped particles of the original powder were melted into beads of nearly spherical shape, as was shown earlier by electron microphotographs[1].
Both the CdS crystals and the spheres were surface contaminated:

the CdS crystals by possible residues from an acetone wash and from handling in air
the spheres by tungsten, surface oxidation and from handling in air.

EQUIPMENT AND PROCEDURE

For the adhesion measurements the ultracentrifuge technique[1] was used. The essential part of the ultracentrifuge is the rotor on the periphery of which the CdS substrates (about 1 mm^2) are fixed by an electrically conductive adhesive. The substrates were then dusted in vacuo with the Zr-coated spheres. Prior to centrifuging, photomicrographs were taken to determine the sphere coverage of the substrates. The dusted substrates were then subjected to centrifuging at accelerations which were increased in steps. After each step, the substrates were photomicrographed in order to determine the percentage of spheres still adhering. Only single spheres of regular shape lying on a flat substrate area were counted. Adhesive forces were measured in the dark and in the presence of green light ($\lambda^5 = 522$ nm) of different intensities of the order of 5.10^{-7} W/cm^2. The substrates were illuminated through a window in the vessel, in the interior of which the centrifuge runs in a vacuum of about 10^{-4} torr. The effective light intensity acting on the spinning sphere-covered CdS has not been measured.

RESULTS

Table I summarizes the results of the measurements. For the different experimental conditions, the median values of the measured adhesive forces divided by the median radii are given. Two size fractions of the spheres were used with median sphere radii of 1.5 and 2.5 μm respectively. Also the conductivities are recorded. Whereas, with specimen A, adhesion increases uniformly with light intensity, there is a minimum of adhesive strength with specimen B at small light intensity. The analysis that follows allocates the densities of states and interprets the forces.

TABLE I

Light-modulated adhesive forces of Zr-coated gold spheres on CdS single crystals.

	CdS crystal			
	specimen A		specimen B	
Experimental conditions	Conductivity (ohm^{-1} . cm^{-1})	$\frac{F}{R}\left(\frac{\text{dyn}}{\text{cm}}\right)$	Conductivity (ohm^{-1} . cm^{-1})	$\frac{F}{R}\left(\frac{\text{dyn}}{\text{cm}}\right)$
Dark	$2 . 10^{-11}$	109 ± 18	$5 . 10^{-11}$	223 ± 10
Small light intensity	$3 . 10^{-8}$	159 ± 21	$2.6 . 10^{-8}$	168 ± 8
Large light intensity	$1.1 . 10^{-6}$	276 ± 7	$1.3 . 10^{-5}$	210 ± 10

DISCUSSION

Qualitatively, the results can be explained on the basis of a simplified energy scheme as used in solid state physics for a metal-semiconductor contact. The energy scheme is shown in Figure 1. The system presented here is assumed to be in a quasi-thermal equilibrium both in the presence and the absence of light. It is further assumed that the system can be dealt with as a one-carrier

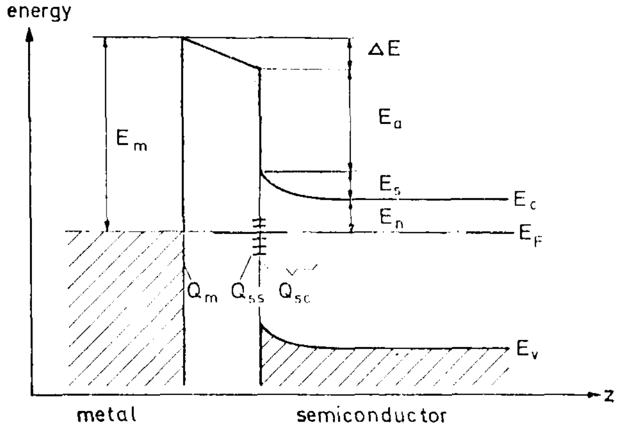

FIGURE 1 Energy scheme of the metal-semiconductor interface.

system, i.e. only electrons are being considered. These assumptions seem justified with the material used. Ion migration is excluded as is mentioned in the concluding remarks.

The force of attraction of the electrostatic double layer at the interface depends on the potential drop ΔE which we calculate with the aid of the energy balance and the charge balance. According to the notation of Figure 1 the energy balance is

$$E_m - (\Delta E + E_a + E_s + E_n) = 0 \tag{1}$$

For the charge balance we take into account that the experiments can only be interpreted with the assumption that the charge density Q_{ss} in surface states is small compared with the charge density Q_{sc} in the space charge below the surface. If the surface state charge density were large, the Fermi level would be fixed at the surface; hence it would not be possible to change the thermal work function and thus the electrostatic double layer adhesion by illumination.

If $Q_{ss} \ll Q_{sc}$, the charge balance yields

$$Q_m - Q_{sc} = 0 \tag{2}$$

From the Gaussian theorm it follows

$$Q_m = -\frac{\varepsilon_0 \Delta E}{ez} \tag{3}$$

where $\Delta E/ez$ is the electrical field strength between the surfaces of the adhering solids.

If an energetically uniform trap distribution n_t in the energy gap is assumed, the integration of the Poisson equation yields the following approximate relation:[6]

$$Q_{sc} \approx \left[\frac{e^2\varepsilon\varepsilon_0}{kT}(n_b + n_t)\right]^{1/2} E_s = \frac{E_s}{L} \tag{4}$$

where

$$L = \left[\frac{\varepsilon\varepsilon_0 kT}{e^2(n_b + n_t)}\right]^{1/2} \tag{5}$$

Here n_b is the free electron concentration in the undisturbed bulk. In our case n_b is calculated from the measured conductivity

$$\sigma = e\mu_n n_b \tag{6}$$

We will later suggest

$$n_t \gg n_b$$

Equations (1) to (4) yield the energy difference

$$\Delta E \approx \frac{E_m - (E_n + E_a)}{1 + (L/\varepsilon z)} \tag{7}$$

L is the effective Debye length and z the normal distance between any two points on particle and substrate.

The attractive force F_{el} between a spherical metallic particle and a flat semiconductor surface follows by simple integration of the capacitor formula

$$\mathrm{d}F_{el} = \tfrac{1}{2}\varepsilon_0 \left[\frac{\Delta E}{ez}\right]^2 \mathrm{d}f \tag{8}$$

where $\mathrm{d}F_{el}$ is the attractive force between the two infinitesimally small plates of the area $\mathrm{d}f$; the electrical field strength between the plates is $(\Delta E/ez)$ (cf. Eq. 7). Integration of Eq. (8) yields the following approximate expression for the electrostatic double layer component of the attraction between a plane substrate (semiconductor) and a spherical particle (metal)[3];

$$F_{el} \approx \frac{\pi\varepsilon_0}{e^2}\frac{R}{z_0 + L/e}[E_m - (E_a + E_n)]^2 \tag{9}$$

This relationship will be compared with the adhesion data. The quantities E_n and L are functions of the illumination.

From references 3, 6

$$n_b = N_c \exp[E_n/kT] \tag{10}$$

and Eq. (5) it follows

$$E_n = kT \ln(eN_c\mu_n/\sigma) \tag{11}$$

The chemical potential E_n and the Debye length L decrease with increasing conductivity, i.e. with increasing light intensity. All other properties remain constant.

Provided that the trap density n_t is larger than the free electron density $n_b(n_t \gtrsim 10^{14}\ \mathrm{cm}^{-3})$, the Debye length L remains constant as well.

The experimental results described in this paper can be interpreted with the aid of (11) and (9). The measured conductivity σ and Eq. (11) render the chemical electron potential E_n which is inserted in (9). Here, $z_0 + L/e$ and $E_m - E_a$ are considered as constants which we adjust to fit with the experimental results.

According to Eq. (9), illumination may lead to an increase or decrease of the adhesive force, depending on whether E_m is larger or smaller than $(E_a + E_n)$. In the latter case, F_{el} may have a minimum as a function of E_n.

In order to account for the measurements with specimen A, we must assume that its flat band-work function $(E_a + E_n)$ was smaller than the work function E_m of the metal. Hence, the adhesive force increased monotonically with increasing light intensity.

In the dark, the work function of specimen B, however, was obviously

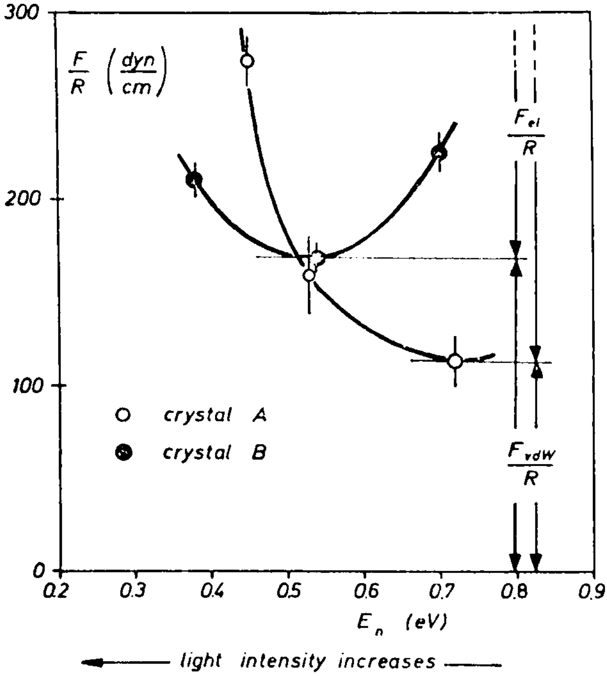

FIGURE 2 Adhesive force F over the particle radius R versus chemical potential E_n of the electron for the system CdS/Zr.

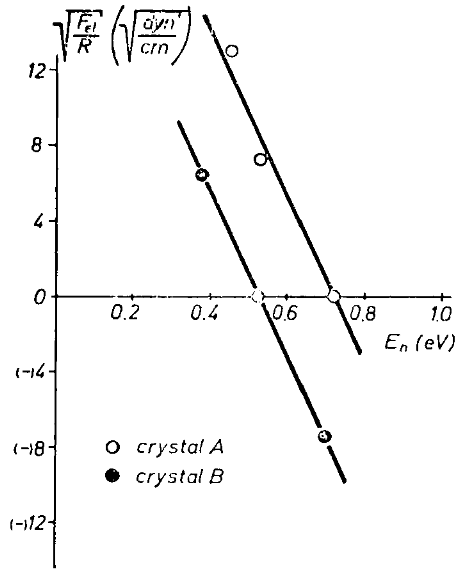

FIGURE 3 (F_{el}/R) versus E_n.

larger than that of the metal. With increasing light intensity the flat band-work function of the photoconductor was reduced until the work functions of the two adherents were equal so that the electrostatic component vanished. On increasing the light intensity further, the difference in work functions became non-zero again so that the electrostatic adhesion component increased.

The constant van der Waals component can be separated from the results of the measurements summarized in Table I, as shown in Figure 2. The proportionality between $(F_{el})^{1/2}$ and E_n implied by this model is illustrated in Figure 3.

The experiments demonstrate the significant effect of electrostatic double layer forces on adhesion. By light variation the adhesive force is changed by a factor of up to 3.

CONCLUDING REMARKS

1) Both the metal spheres and the CdS single crystals were surface contaminated. At least the spheres had micro-asperities on their surfaces. This, we think, accounts for the observed difference in work functions and van der Waals adhesion (cf. Figure 2) between specimens A and B. This also explains, at least in part, that in order to account for the measured electrostatic

force the Debye length L in (9) has to be unrealistically small. Attempts at reconciling theory with experiment must, above all, take the microgeometry (asperities) at the contact into account.

2) It may be argued that the adhesion change may be due to photo-chemical surface reactions at the CdS. This is ruled out by the following reference experiment: When red quenching light (870 to 2750 nm, $5 \,.\, 10^{-2}$ W/cm^2 intensity outside the centrifuge window) was added to the green light, the dark values both of conductivity and adhesion were found.

Acknowledgement

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LIST OF SYMBOLS

E_a	electron affinity of the semiconductor
E_c	lower conduction band edge
E_F	Fermi level
E_m	work function of the metal
E_n	chemical potential of the electrons, i.e. the distance between the quasi-Fermi level E_{Fn} of electrons and the lower conduction band edge E_C in the undisturbed volume of the semiconductor
E_s	band bending at the semiconductor surface
E_V	upper valence band edge
$E_a + E_n$	flat band work function of the semiconductor
ΔE	difference of work functions
F	attractive force between undeformed sphere and half-space
F_{vdW}	van der Waals force
F_{el}	electrostatic double layer force ($F \equiv F_{vdW} + F_{el}$)
L	Debye length
N_c	effective state density at conduction band edge (2.10^{18} cm^{-3})
Q_m	charge on metal surface
Q_{sc}	space charge
Q_{ss}	charge in surface states
R	particle radius
T	absolute temperature
e	electron charge
f	area
k	Boltzmann constant
n_b	electron concentration in the undisturbed volume of semiconductor

n_t	trap concentration, uniform distribution over the energy gap assumed
z	distance between sphere and substrate
z_0	smallest equilibrium distance between sphere and substrate
ε	relative dielectric constant, $\varepsilon(\mathrm{CdS}) = 10$
ε_0	dielectric constant of vacuum
λ	wavelength of light
μ_n	electron mobility (μ_n (CdS) $\approx 100\ \mathrm{cm^2/Vs}$)
σ	conductivity

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