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PHYSICAL REVIEW B VOLUME 3, NUMBER 12 15 JUNE 1971

Dielectric Theory of the Barrier Height at Metal-Semiconductor and Metal-Insulator Interfaces

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The barrier height at metal-semiconductor and metal-insulator interfaces is calculated for a simple model of the system, in which the metal is replaced by a jellium model and the semiconductor and insulator by a continuum with a static dielectric constant. The spreading out of electronic charge into the dielectric continuum is determined by a variational procedure, which is an extension of the Smith's theory of the work function. Approximately, the calculated barrier height increases linearly with the work function of the metals. The slope increases with the ionicity of the semiconductors. The model, however, cannot explain the abrupt covalent-ionic transition.

The dependence of the barrier height ϕ_B at metal-semiconductor and metal-insulator interfaces on the work function ϕ_M of the metal is known to be approximated by the linear relation[1]

$$\phi_B = S\phi_M + \phi_0 , \tag{1}$$

where S and ϕ_0 are constants characteristic of the semiconductor and insulator. The slope S increases with ionicity from 0.1 (covalent materials) to 1 (ionic materials).

Recently it has been suggested by Phillips[2] that a theory of the barrier height may do without the knowledge of surface states. In this paper we consider the problem in the same spirit, but from a different point of view. We simplify the problem by introducing a model of the metal-semiconductor and metal-insulator systems, that is, a jellium model for the metal and a "dielectric continuum" model for the semiconductor and insulator. In the jellium model the positive charges are replaced by a uniform background of density

$$n_+(z) = n_+ , \quad z \le 0 . \tag{2}$$

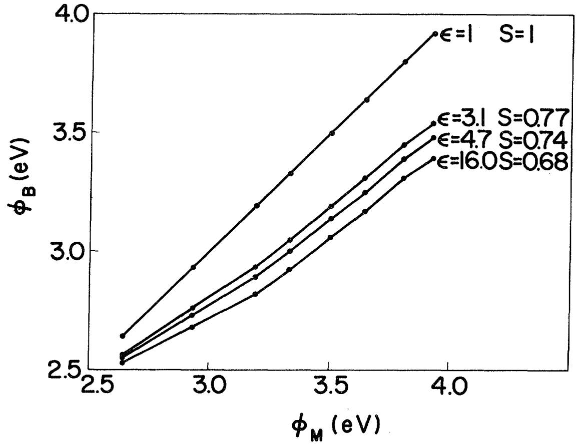

FIG. 1. Barrier height vs calculated work function of metals. Estimated slope is shown in the figure.

In the dielectric continuum model, the semiconductor and insulator are replaced by a continuum with the static dielectric constant ϵ. We assume that the electron number density $n(z)$ has the following form, as in the work of Smith[3]:

$$n(z) = n_+ - \tfrac{1}{2} n_+ e^{\beta z}\,, \quad z \le 0$$
$$n(z) = \tfrac{1}{2} n_+ e^{-\beta z}\,, \quad z > 0 \tag{3}$$

where β is a variational parameter and describes the spreading out of the electronic charge into the dielectric continuum. The corresponding Coulomb potential is

$$\phi(z) = \frac{2\pi n_+}{\beta^2}\, e^{\beta z} - \frac{2\pi n_+}{\beta^2}\left(1 + \frac{1}{\epsilon}\right), \quad z \le 0$$
$$\phi(z) = -\frac{2\pi n_+}{\epsilon\beta^2}\, e^{-\beta z}\,, \quad z > 0\,. \tag{4}$$

Thus β can be determined by Eq. (2.11) of Ref. 3, where the first term should be replaced by $\pi(1+1/\epsilon)n_+^2/4\beta^3$. The barrier height is, in atomic units,

$$\phi_B = \frac{2\pi n_+}{\beta^2}\left(1 + \frac{1}{\epsilon}\right) + \left(\frac{3}{\pi}\right)^{1/3} n_+^{1/3} + \frac{0.056 n_+^{2/3} + 0.0059 n_+^{1/3}}{(0.079 + n_+^{1/3})^2} - \tfrac{1}{2}(3\pi^2)^{2/3} n_+^{2/3}\,. \tag{5}$$

Smith's work function is a special case with $\epsilon = 1$.

Calculated results are shown in Table I and Fig. 1. The estimated slope (Fig. 1) increases with ionicity in agreement with experiments, but the value is too large for the covalent materials and too small for the ionic materials. A preliminary calculation including the Friedel oscillations gives smaller values to the slope of the covalent materials than those estimated here. It should be noted, however, that the potential of the interface double layer changes smoothly with the change of the static dielectric constant, and thus the static dielectric constant by itself cannot describe the dramatic covalent-ionic transition.[1]

TABLE I. Barrier height ϕ_B (in eV) and spreading-out constant β (in a.u.). Values of n_+ (in 10^{-3} a.u.) and ϵ are taken from Refs. 2 and 3. The value of β is shown in parentheses. The third column for vacuum is the result obtained by Smith (Ref. 3).

	ϵ n_+	Vacuum 1	Al_2O_3 3.1	SiO_2 4.3	GaSe 4.7	CdSe 5.8	CdTe 7.2	AlAs 10.3	Si 12.0	Ge 16.0
Cs	1.33	2.64 (1.33)	2.56 (1.29)	2.55 (1.28)	2.55 (1.28)	2.54 (1.28)	2.54 (1.28)	2.54 (1.27)	2.53 (1.27)	2.53 (1.27)
Na	3.77	2.93 (1.27)	2.76 (1.17)	2.73 (1.16)	2.73 (1.16)	2.71 (1.15)	2.70 (1.14)	2.69 (1.13)	2.69 (1.13)	2.68 (1.13)
Au	8.80	3.19 (1.23)	2.93 (1.07)	2.89 (1.04)	2.89 (1.04)	2.87 (1.02)	2.85 (1.01)	2.84 (1.00)	2.83 (1.00)	2.82 (0.99)
Mg	12.8	3.33 (1.22)	3.05 (1.04)	3.00 (1.01)	3.00 (1.01)	2.98 (0.99)	2.96 (0.98)	2.94 (0.97)	2.93 (0.96)	2.92 (0.96)
Zn	19.5	3.50 (1.22)	3.19 (1.03)	3.15 (1.00)	3.14 (0.99)	3.12 (0.98)	3.10 (0.97)	3.08 (0.95)	3.07 (0.95)	3.06 (0.94)
Al	26.9	3.64 (1.24)	3.31 (1.03)	3.26 (1.00)	3.25 (1.00)	3.23 (0.98)	3.21 (0.97)	3.19 (0.95)	3.18 (0.95)	3.17 (0.94)
Ta	41.3	3.80 (1.27)	3.45 (1.05)	3.40 (1.02)	3.39 (1.01)	3.37 (1.00)	3.35 (0.98)	3.33 (0.97)	3.32 (0.96)	3.31 (0.95)
Mo	57.4	3.92 (1.30)	3.54 (1.07)	3.49 (1.04)	3.48 (1.03)	3.45 (1.02)	3.44 (1.00)	3.41 (0.98)	3.40 (0.98)	3.39 (0.97)

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PHYSICAL REVIEW B VOLUME 3, NUMBER 12 15 JUNE 1971

Selection Rules for Circularly Polarized Waves in Nonlinear Optics

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The symmetry properties of nonlinear optical susceptibilities in the electric dipole approximation for collinear circularly or elliptically polarized light waves have been analyzed on the basis of group-theoretical considerations. Selection rules are obtained for the nonlinear interaction of arbitrary order along any symmetry axis of the 32 crystallographic groups and the three-dimensional rotation group.

I. INTRODUCTION

It is well known that nonlinear optical interactions in crystalline substances are dependent on both the symmetry properties of the medium and the state of polarization of the interacting radiation. With respect to the latter, the primary research emphasis has been in considering the radiation to be linearly polarized. In the last few years, however, there has been an increasing interest in the use of circularly polarized waves in nonlinear processes. First, the anticipated selection rules involving circularly polarized radiation for both second- and third-harmonic generation have been substantiated.[1–4] For example, a circularly polarized laser wave produces a second harmonic with opposite sense of circular polarization along a threefold axis, and no third harmonic can be produced in an isotropic medium using circularly polarized radiation. In addition, harmonic generation employing circularly polarized laser radiation has been recently correlated with the unique symmetry properties of a liquid-crystal medium.[5] Second, the question of conservation of angular momentum of nonlinear interactions of circularly polarized waves has been investigated.[6] Third, circular birefringence may be employed in phase matching a nonlinear optical interaction,[1,7,8] and this technique has been applied to difference-frequency generation in the far infrared.[9] Fourth, the use of circularly polarized waves in third-harmonic generation has resulted in a new measurement of the time duration of picosecond optical pulses.[10]

In Table I a summary is presented of experimental results for the nonlinear interactions of circularly polarized radiation. The media employed, the corresponding symmetry group, and the axis of symmetry in the direction of propagation are indicated. All these results are in agreement with the theoretical predictions discussed in the various references cited. Previous theoretical work in accounting for the behavior of nonlinear interactions of circularly polarized waves has been based primarily upon explicit calculations from the known forms of the second- and third-order nonlinear susceptibilities or of the crystal field for particular point groups. These results have been obtained to third order in the nonlinearity.[1,2] The connection between these selection rules and the conservation of angular momentum have been discussed in detail by Bloembergen.[2,6]

In this paper, a general method of obtaining the selection rules for the nonlinear interactions of collinear circularly polarized waves has been developed using group-theoretical considerations. It has similarly been applied to collinear elliptically polarized waves. The method is described in Sec. II and applied to all 32 point groups and the three-dimensional rotation group and it is applicable to any order in the nonlinearity. Furthermore, this treatment leads to the prediction of the existence of recursion relations connecting the polarization behavior of lower- and higher-order processes. The results are summarized in Sec. III.

To avoid any possible misunderstanding later, we emphasize that, when we discuss the cases involving circularly polarized fundamental waves, we consider the fundamental wave which is normally incident upon the crystal to be circularly polarized and ask the question whether a particular harmonic