ELECTRONIC CONDUCTION IN LIPID FILMS WITH METAL CONTACTS

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ABSTRACT The electrical characteristics of lipid films with Au and Hg contacts were investigated. Our results indicate that the conduction is mainly electronic and is electrode limited. With gold biased negatively, the current-voltage characteristics of thin and thick films follow the equations: $I = 4.367 \exp [9.58(eV + 0.21)^{1/2}] \cdot [1 - \exp(-eV/kT)]$pA, and $I = 3.424 \exp [8.59(eV + 0.082)^{1/2}][1 - \exp(-eV/kT)]$pA, respectively. For thick films, the conductivity is insensitive to thickness. By temperature and photoresponse measurements the interface barrier height is found to be 1.09 eV. In view of the possible structural disorders in the films, a model is proposed to explain our findings based on the theory of noncrystalline materials. According to this model, the band gap for the film is 2.016 eV and the density of localized states is near the Fermi level, 1.31×10^{18} cm^{-3} eV^{-1}. The results may be helpful in providing some insight into the speculated electronic conduction in biological membranes.

INTRODUCTION

In aqueous media, oxidized cholesterol has been found to be able to form very stable thin lipid films (1), which are excellent models for biological membranes. These films are about 40–50 Å thick and have extremely high resistivity. Therefore they form a new class of thin film systems, in addition to metal-insulator-metal and metal-insulator-semiconductor structures. Rosenberg et al. (2) have been able to show that, in the presence of certain ions, electronic conduction is possible in the oxidized cholesterol films. In spite of several tentative explanations (3–4), the exact mechanism of electron transport through the film is still obscure and the question of whether the current is interface limited or bulk limited remains unanswered. The fact that investigation of electrical characteristics of a metal-insulator-metal sandwich has been able to offer some insight into the current flow mechanisms in thin insulating films (for example, see reference 5) prompted us to study the electrical properties of the Au-lipid-Hg system. Electrical conduction in thin insulating films is a very complicated process and encompasses several possible mechanisms: space-charge limited process, hopping, tunneling, internal field emission, Schottky emission, and Poole-Frenkel effect (6). Under various conditions, one or several of these processes might dominate over the others. It was found that, in the presence of high field, for example between 10^4 and 10^6 V/cm (7), and at high temperature, the Schottky effect is responsible for the current transfer in the Au-polymerized silicone oil, Al-Al_2O_3, Al-GeO_3 (8) junctions and in a number of organic insulating materials (9).

Junctions between metals and fatty acid monolayers have been used for electrical measurements. Several conduction mechanisms including tunneling and thermionic emission have been proposed to account for the observed results (10). The purpose of this paper is to report some of our recent studies on the junctions between metals and monolayers formed from oxidized cholesterol. After careful analysis our results indicate that the Schottky effect is the rate-limiting process. A model is proposed and some of the parameters of the electronic structure of the film are evaluated based on the experimental results.

EXPERIMENTAL PROCEDURES

The films were formed according to the Langmuir-Blodgett process (11–14). The lipid solution was first prepared by bringing a 4% cholesterol solution in *n*-octane to its boiling point and bubbling molecular oxygen through for 8 h (1). The apparatus consisted of a Plexiglas trough (3 × 12 × 18 inches) and a balance. They were first degreased and then cleaned in running tap water for 24 h and, subsequently, in deionized (DI) water. After this, the trough was filled with DI water. No attempts have been made to determine the effects of pH value and the salt content on the formation of the lipid monolayers. Using a syringe equipped with a precision repeating dispenser, the lipid solution was deposited on the aqueous surface. Under illumination, a very colorful pattern appeared as a result of light interference. After deposition, it was allowed for evaporation of the lipid solvent. Compressing of the monolayer was achieved by putting weights on the balance. It should be noted that too much weight on the balance can cause the monolayer to collapse whereas voids in the monolayer are inevitable if weight is not enough.

The base electrode (Au) on the glass slides was prepared by vacuum deposition through a mask, which was made of stainless steel, 0.002 inches thick, by photoetching technique using Kodak KMER. The evaporation was done at a pressure of about 10^{-6} Torr, and the thickness of the gold was about several thousand angstroms.

The transferring of the monolayer from the trough to the slide was achieved by slowly dipping the latter through the lipid/aqueous interface and withdrawing from it. There were two monolayers deposited on the glass slide with one downward and upward trip. The dipping motion was extremely slow to allow for drying of glass slide, and it was controlled by a micromanipulator. It is obvious that the thickness of lipid layers on the electrode is determined by the number of trips it makes. Experiments done on thinner films (one or two monolayers) were not successful, apparently due to inhomogeneities or voids. A metal/lipid junction thus prepared is shown in Fig. 1. There are nine different electrodes on each glass slide. By dipping it into the trough at three different levels, we have three different thicknesses, each having three electrodes (Fig. 2). Therefore nine sets of experiments could be done on a single slide.

Mercury was used as the counterelectrode. This was found to be quite successful (15) because it tends to bridge small defects in the layers to its high surface tension. Early attempts of making countercontacts by evaporating metal onto the lipid layer resulted in short-circuited samples, obviously because of the penetration of metal atoms through the film.

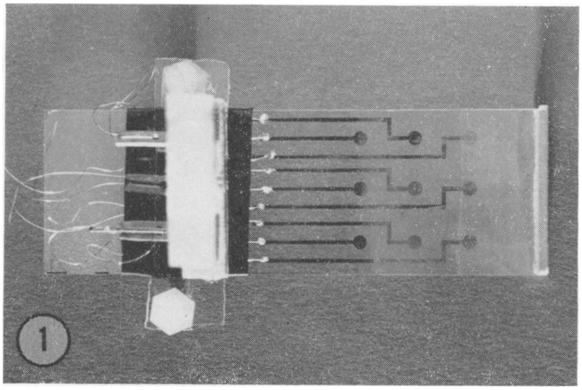

FIGURE 1

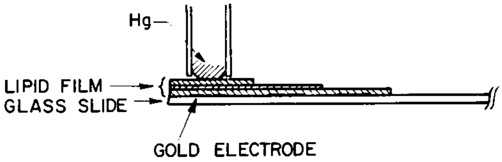

FIGURE 2

FIGURE 1 Picture of the sample
FIGURE 2 Schematic diagram of the Au-lipid-Hg junctions.

The thickness of the films was measured by evaporating a highly reflective aluminum layer on the sample and then observing the interference of monochromatic light through an Angstrom scope interferometer (Varian Associates, Palo Alto, Calif.). Except for small areas, the thickness of the lipid layer was found to be quite uniform. As we shall see, the resistivity of the film is very sensitive to atmospheric moisture. Therefore, in the process of making measurements, the sample was kept in a metallic enclosure with dry nitrogen gas passing through.

EXPERIMENTAL RESULTS

Since in many cases the conductivity of organic materials depends strongly on the moisture in atmosphere, we first study this effect on our samples. The humidity of the environment was controlled by bubbling nitrogen gas through an Erlenmeyer flask containing distilled water, then passing it through a metallic enclosure in which the sample was kept. The flow rate of the nitrogen gas was adjusted by a flow meter. The variation of current with time at a bias of 50 mV (Au negative) was measured and is shown in Fig. 3. It can be seen that the current increases several orders of magnitude, from 10^{-10} to 10^{-7} A, and reaches a saturation value. One plausible explanation for this result is that the conductivity is affected by the water content in the sample. As more moisture is adsorbed, the conductivity increases. Similar results have been observed in protein (16). Because of the above finding, the samples were kept in a dry environment provided by passing dry nitrogen through. The results reported below are for dry samples.

The current-voltage characteristics were measured on films of different thicknesses. They are generally asymmetrical (see Fig. 4). In the low voltage range, when Au electrode is biased positive, the incremental resistivity is lower than when it is biased negative. In the high voltage range, the reverse is true. Only the conduction mechanisms in these junctions for Au electrode negatively biased with respect to Hg electrode are investigated.

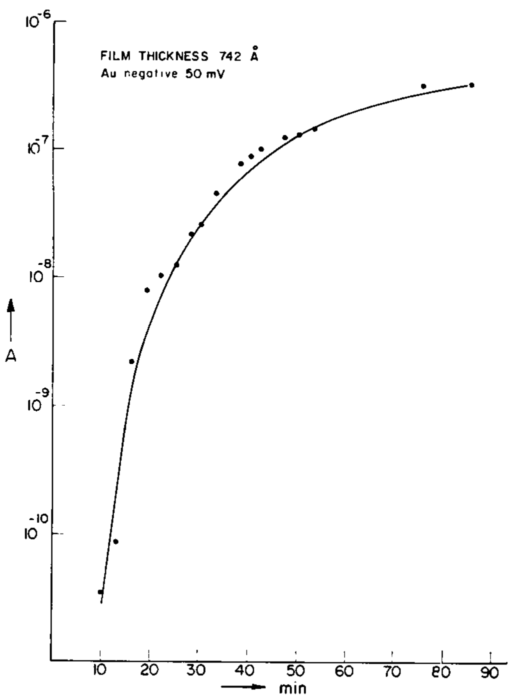

FIGURE 3

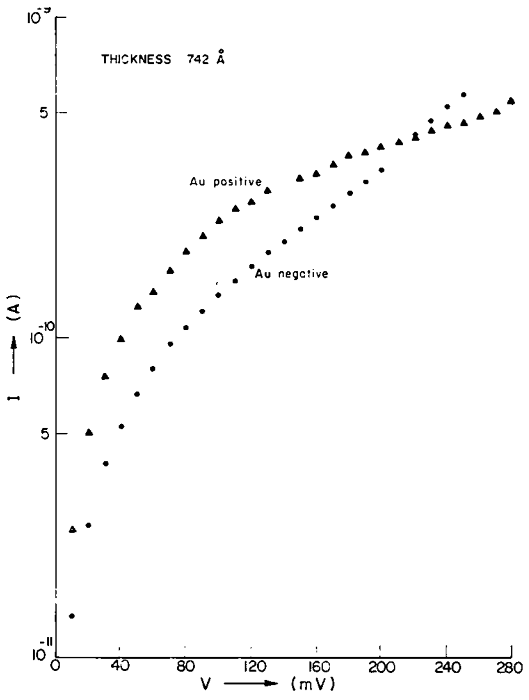

FIGURE 4

FIGURE 3 Increase in conductivity due to adsorption of atmospheric moisture.
FIGURE 4 Current-voltage curves showing asymmetry.

The *I-V* curves of the films with different thicknesses are shown in Fig. 5. The current-voltage relationships are nonlinear. There exist the breakdown voltages (indicated by arrows in Fig. 5) which were observable as the junctions abruptly became shorted and the gold electrodes turned white by forming an amalgam with mercury. This phenomenon is apparently due to disruption of the molecular bonds which resulted in diffusion of Hg through the film. Therefore this kind of breakdown is irreversible. At high voltages before breakdown, there seems to be a discontinuous increase of current with voltage. Although there is a dependence of conductivity on thickness, the *I-V* curves for thin and thick films show the same pattern. It is interesting to note that, for thicker films, the thickness seems to have an insignificant effect on conductivity (17).[1]

The dependence of current on temperature ranging from −5 to 55°C at constant bias (Au electrode negative 150 mV) was also measured, and the result is shown in Fig. 6. A large dependence is observed, which implies that electrical conduction is thermally activated. Plots of log (I/T^2) vs. $1/kT$ give straight lines, except at lower temperatures. The activation energies given by the slopes are 1.01, 1.03 eV for films

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[1] Similar results were observed in films formed from red cell lipids in *n*-decane.

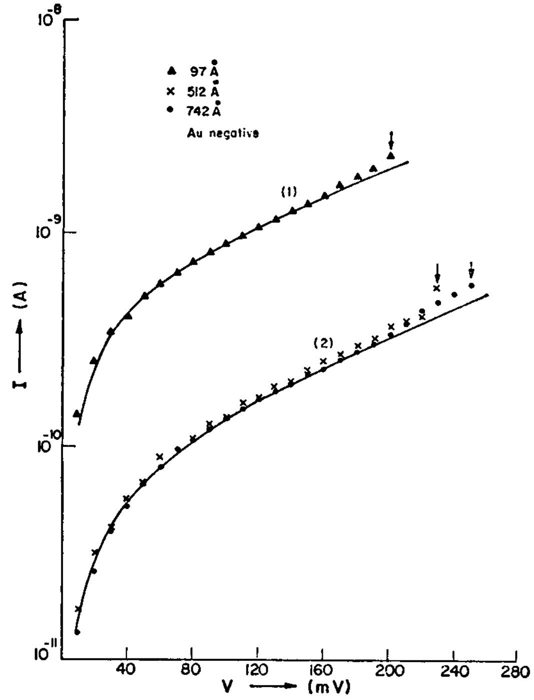

FIGURE 5

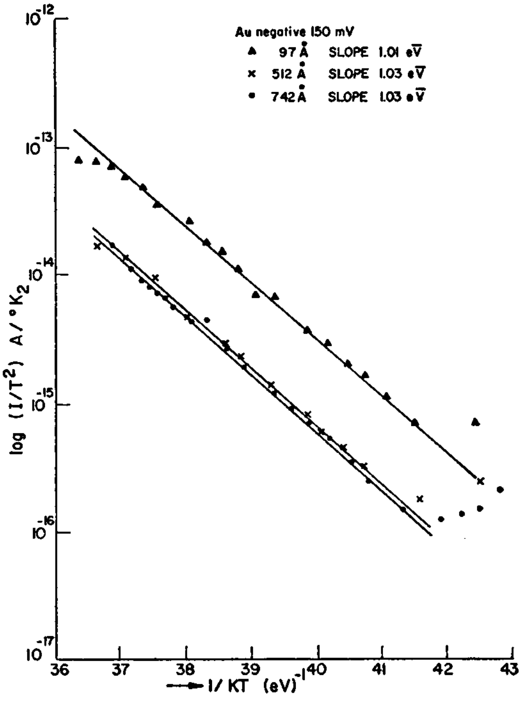

FIGURE 6

FIGURE 5 Current-voltage characteristics of the films. Solid line (1) $I = 4.367 \exp [9.58 (eV + 0.21)^{1/2}][1\text{-}\exp(-eV/KT)]$ pA. Solid line (2) $I = 3.424 \exp [8.59 (eV + 0.082)^{1/2}] [1 - \exp(-eV/KT)]$pA.

FIGURE 6 Temperature dependence of the current

of thicknesses 97, 512, 742 Å, respectively. They do not vary very much between thick and thin films. At lower temperatures, the films exhibit anomalous behaviors. That is, the conductivity increases with decreasing temperature, a phenomenon well known in metals for the phonon scattering of electrons. The same result was observed on the measurement of the sheet resistance of lipids (unpublished results).

DISCUSSION

First we have to identify the nature of the charge carriers, whether they are ionic or electronic. Since the current in the metal electrodes is carried by electrons, if the conduction were ionic, oxidation and reduction would have to take place at the metal/lipid junctions. Both of these processes would suggest depletion of ions inside the film and hence a diminishing current with time. However, no significant change in current was found with the junction biased for more than 48 h. This fact alone indicates that the dominant carriers are electrons rather than ions.

Next we would like to know whether the current is electrode limited or bulk limited. From the experimental result, the current-voltage characteristics are asymmetric, and for thicker films, the conductivity is independent of thickness. Also, the temperature measurement gives the value of activation energy which is the same for both thin and thick films. This implies a barrier height which is independent of the spacing of the electrodes. All these data strongly suggest that the current is electrode limited.

When the Au electrode is biased negative, electrons are injected into the film, either by field-enhanced thermionic emission (Schottky emission) or by direct tunneling through the interface energy barrier into the conduction band of the film. Tunneling is eliminated from consideration in view of the strong temperature dependence observed. Hence the most probable conduction mechanism is by Schottky emission.

To those who are unfamiliar with Schottky emission and tunneling, a brief account given below might be helpful. For an electron to escape from a metal into vacuum, for example, it must surmount the surface barrier (ψ). A simple way of energizing the electrons to do this is to heat the metal as is usually done in an electric lamp or in a vacuum tube. This is called thermionic emission. In a diode, electron emission from the cathode is further assisted by the field at the cathode surface in the direction of pulling electrons out. The field and the image force work together to lower surface barrier. This effect is called the Schottky effect. It can be easily shown (6) that the electron emission or Schottky emission current follows $I = AT^2 \exp(-\psi/kT) \exp[b(V^{1/2})/kT]$ where T is the absolute temperature and V, the applied potential. We shall have more to say about Schottky emission later on.

Electron tunneling is a quantum mechanical process and has no classical counterpart. When a barrier is thin enough, say less than 50 Å, and when the applied field is strong enough, say greater than 10^6 V/cm, an electron has a certain probability of tunneling through the barrier without going through the process (classical) of being thermally activated and jumping over the barrier as it does in thermionic emission. The situation may be likened to a voltage wave passing through a discontinuity in a transmission line. The discontinuity could greatly attenuate the wave but does not completely stop it. Because we shall not be concerned with tunneling in this paper, further discussion is unwarranted.

Since we have dissimilar electrodes, the intrinsic fields (18) should be included in our consideration. The current-voltage relationship for Schottky emission is well known and is given by (19):

$$J = AT^2 \exp\left[\frac{-(\psi_{\text{Au}} - \psi_i)}{kT}\right]\left[1 - \exp\left(-\frac{eV}{kT}\right)\right], \tag{1}$$

where A is the Richardson constant, T is the absolute temperature (kT in electron volts), ψ_{Au} is the intrinsic barrier height at the Au/lipid interface, ψ_i is the lowering of barrier by the electron image force, and V is the biased voltage (positive when Au is negatively biased).

For thin films with thickness less than 100 Å, after taking into account of the effect of multiple images (20),

$$\psi_i = \left[\frac{14.4(eV + \Delta\psi)}{\epsilon l}\right]^{1/2} \text{eV}, \tag{2}$$

where $\Delta\psi$ is the intrinsic potential difference (in electron volts), ϵ, the high frequency dielectric constant of the film (in absolute unit), and l, the thickness of the film (in angstroms). Substituting Eq. 2 into Eq. 1, we have,

$$J = AT^2 \exp\left(-\psi_{\text{Au}}/kT\right) \exp\left\{[14.4\,(eV + \Delta\psi)/\epsilon l)^{1/2}/kT\right\}[1 - \exp\left(-eV/kT\right)]$$

$$\text{(thin film).} \tag{3}$$

For thick films,

$$\psi_i = \left[\frac{eV + \Delta\psi}{4\Pi\epsilon\epsilon_0 d}\right]^{1/2} \times 10^5\ \text{eV}, \tag{4}$$

where ϵ_0 is the dielectric constant in free space (in farads per meter) and d is the distance in which $\Delta\psi$ and the applied voltage develop (in angstroms). Substituting Eq. 4 into Eq. 1

$$J = AT^2 \exp\left[-\frac{\psi_{\text{Au}}}{kT}\exp\right]\left\{10^5\left[\frac{eV + \Delta\psi}{4\Pi\epsilon\epsilon_0 d}\right]^{1/2} \Big/ kT\right\}$$

$$\cdot\left[1 - \exp\left(-\frac{eV}{kT}\right)\right] \quad \text{(thick film).} \tag{5}$$

From Eqs. 3 and 5, it is evident that, for asymmetric junctions with the presence of an intrinsic field, a Fowler plot ($\ln I$ vs. $V^{1/2}$) does not generally give a straight line. Instead, the plot should be $\ln I$ vs. $(eV + \Delta\psi)^{1/2}$. However, $\Delta\psi$ is not known beforehand.

In order to estimate the parameters, we use the least square technique for fitting the two nonlinear Eqs. 3 and 5 to the measured I-V characteristics. The results are, for thin films (the solid lines in Fig. 5),

$$I = 4.367 \times 10^{-12} \exp\left[9.58\,(eV + 0.21)^{1/2}\right][1 - \exp\left(-eV/kT\right)]\ \text{A}, \tag{6}$$

and for thick film (742 Å),

$$I = 3.424 \times 10^{-12} \exp\left[8.59\,(eV + 0.082)^{1/2}\right][1 - \exp\left(-eV/kT\right)]\ \text{A}. \tag{7}$$

From Eq. 6, assuming $\epsilon = 2.5$ (21–22),[2] $l = 94$ Å (thin film), and $\Delta\psi = 0.21$ eV. From Eq. 7 $d = 116.73$ Å (thick film), and $\Delta\psi = 0.082$ eV.

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[2] This is the value evaluated by Ohki (21). Similar values are found in cadmium steorate and cadmium arachidate monolayers (22).

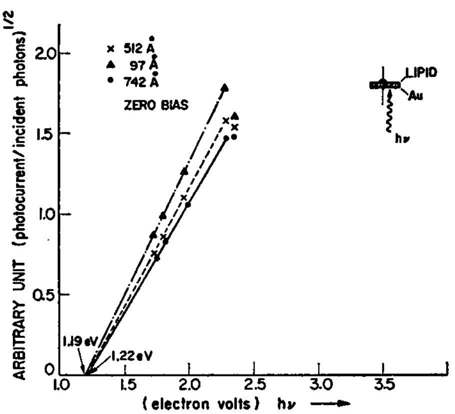

FIGURE 7 Photoresponse characteristics

For thin film, the evaluated l is in excellent agreement with the film thickness (97 Å) measured by interferometer. The value of $\Delta\psi$ is close to the difference of work functions of gold and mercury, that is, 4.76 − 4.53 = 0.23 eV (23). However, for thick films, d is vastly different from the spacing of electrodes.

From the temperature-dependence measurement, the activation energies for thin and thick films are, respectively, 1.01 V and 1.03 eV. After compensating for lowering of barriers by the external bias of 150 mV, ψ_{Au} (thin film) = 1.099 eV, and ψ_{Au} (thick film) = 1.081 eV, the average value being 1.09 eV.

The interface barrier height between gold and lipid was also obtained by the usual photoresponse measurement. Photocurrent was generated by shining monochromatic light from 150-W xenon lamp (E. Leitz, Inc., Rockleigh, N. J.) through a monochromator (Bausch and Lomb Inc., Scientific Instrument Div., Rochester, N. Y.) or band-pass filters onto the gold electrode. The square root of the photocurrent per incident photon thus measured is plotted against the light energy in Fig. 7. From Fowler's theory (24), by extrapolating this line to the axis for which $(\text{photoresponse})^{1/2} = 0$, we can obtain the barrier height. The values obtained are 1.19 V and 1.22 eV for thin and thick films, respectively. These seem to be close to but higher than the values from temperature measurement. However, as recently indicated by Lewicki et al. (25) as a result of the scattering of photoexcited electrons into the insulator conduction band, the photoresponse does not follow Fowler's relation at the low energy level. Therefore the extrapolated value is usually larger than the true barrier height. This seems to be the case in our junctions. Just for comparison, the barrier height determined by photoresponse is 2.2 eV for aluminum-polymer film sandwich which displayed a bulk-limited (26) current transport.

Based on the above information, the following model is proposed to explain the observed results. Before the metal electrodes and the film come into contact, the situation is shown in Fig. 8 *a*. They have the same vacuum level. In the film itself, disorders should be expected; they either are translational or result from deviation

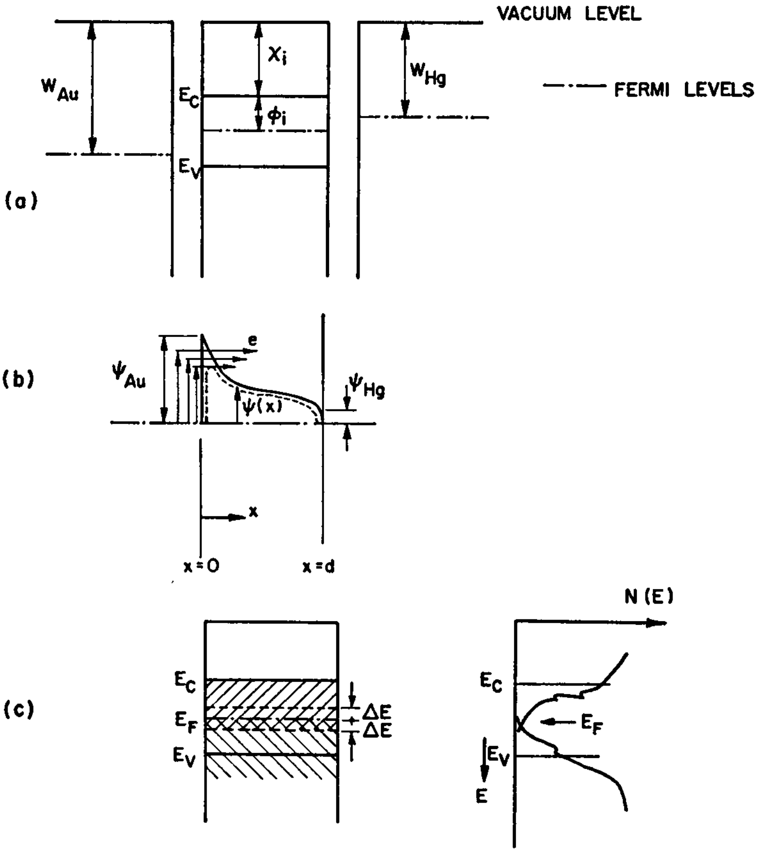

FIGURE 8 (*a*) Energy diagram before contact is made between lipid and the metals. (*b*) Energy diagram of the Au-lipid-Hg junction. Dotted line shows the lowering of energy barrier by image charges. (*c*) Schematic diagram showing density of states. The states between E_c and E_v are localized.

from stoichiometry. As is generally known, the electron wave functions near the band edges are strongly perturbed by the structural disorders and become localized (27).[3] They give rise to tailing of density of states well into the gap, and overlapping of valence and conduction bands may or may not occur. We assume this happens in our model. In the presence of foreign atoms which may give rise to donor or acceptor states, there may be humps in the density of states as a result of the dangling bonds. When in the localized states in the gap, the electrons are essentially immobilized. Therefore, these states are, in fact, traps. It is generally believed that the Fermi level falls near the center of the gap where the total density of states is near its minimum. Also, the valence band states are neutral when occupied and conduction band states are neutral when empty (28). This means that the valence band

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[3] Also see discussion in Mott and Davis (reference 29, chapter 2).

states above the Fermi level (E_F) are positively charged, whereas the conduction band states below E_F are negatively charged. The density of states for the film is schematically shown in Fig. 8 *c*.

When the electrodes and the film come into contact, because of the difference in work functions there will be a transient flow of electrons in and out of the film into the metals. The process will stop when the film Fermi level coincides with the electrode Fermi levels. As a result of this charge injection, the bands will be distorted (Fig. 8 *b*).

We shall assume that the density of states at the tail is uniform and is same for valence and conduction bands. Let it be N_t m^{-3} eV^{-1}. From Poisson's equation.

$$d^2\psi/dx^2 = \rho/\epsilon\epsilon_0 , \tag{8}$$

where ρ is the charge density, and ψ is the energy in electron volts measured from E_F to band edge. Initially before the contact is made, neutrality condition is satisfied. However, because of the distortion of the energy band by the contact potentials space charge appears and is equal to

$$\rho = 2e(\psi - \phi_i) \times N_t , \tag{9}$$

where we have neglected the mobile holes and electrons since the Fermi level is usually far away from the band edges E_c and E_v. The factor 2 appears in Eq. 9 because if there is an increase of positive charge there will be a corresponding decrease of negative charge. It is assumed that $| \psi - \phi_i | \leq \Delta E$ (see Fig. 8 *c*) for otherwise there would be a discontinuity.

Eq. 8 becomes

$$\frac{d^2\psi}{dx^2} = \frac{2e(\psi - \phi_i)N_t}{\epsilon\epsilon_0} = \frac{\psi - \phi_i}{\delta^2}, \tag{10}$$

where

$$\delta = (\epsilon\epsilon_0/2\, eN_t)^{1/2}. \tag{11}$$

The solution of Eq. 10 with the boundary conditions at $x = 0$, $\psi = \psi_{\mathrm{Au}}$, and at $x = d$, $\psi = \psi_{\mathrm{Hg}}$, is given by

$$\psi - \phi_i = (\psi_{\mathrm{Au}} - \phi_i)\frac{\sinh[(d - x)/\delta]}{\sinh(d/\delta)} + (\psi_{\mathrm{Hg}} - \phi_i)\frac{\sinh(x/\delta)}{\sinh(d/\delta)}. \tag{12}$$

From the experimental result, $\psi_{\mathrm{Au}} = 1.09$ eV. As there is an intrinsic potential of 0.21 eV in the thin film, ψ_{Hg} should be $1.09 - 0.21 = 0.88$ eV. For thick film we should have flat band condition in the bulk. As the intrinsic potential is 0.082 eV in thick film, the value of ϕ_i should be $1.09 - 0.082 = 1.008$ eV.

Now we would like to estimate roughly what the value of N_t would be. For thick

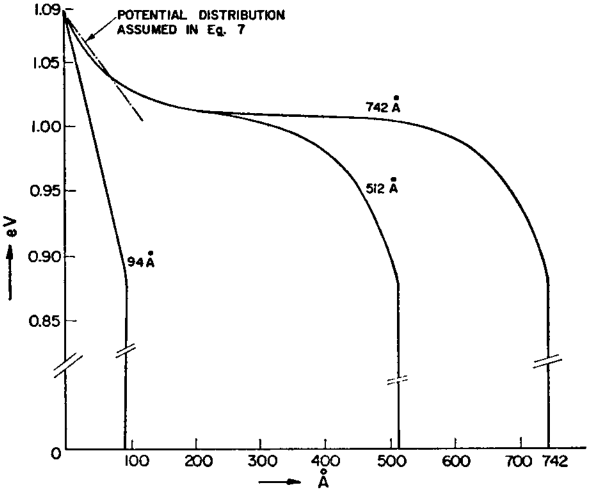

FIGURE 9 Potential profile of the films as calculated from Eq. 12. $N_t = 1.31 \times 10^{18}$ cm^{-3} eV^{-1}, $\phi_i = 1.008$ eV, $\psi_{Au} = 1.09$ eV, $\psi_{Hg} = 0.88$ eV.

films, there is a drop of 0.082 eV in a distance of 116.7 Å. However, the potential distribution follows Eq. 12 instead of being linear function of x as tacitly assumed in Eq. 7. This means the electric field near the gold electrode is higher than the space-charge free value. The l measured from the current-voltage curve is usually less than the actual distance over which the voltage drops. If α is the ratio between the actual distance and the apparent distance, the value was found to be 1.35 for Mylar and 2.25 for polyvinyl formal (9). In our case, we evaluate the value of N_t that would give $\psi = \phi_i + 20\% \times 0.082$ eV at $x = 116.7$ Å (see Fig. 9). The result is $N_t = 1.31 \times 10^{18}$ (cm^3 – eV)$^{-1}$.

The potential profiles based on the estimated values for films of different thicknesses are shown in Fig. 9. For thick films, the space charges due to the presence of localized states screen out part of the field due to the difference in electrode work functions. For thin film, the energy barrier is approximately a linear function of distance and the intrinsic field is higher. The nonlinear potential profile (Fig. 9) in thick films is responsible for the failure of Eq. 7 to give correct value for film thickness.

CONCLUSION

Electrical measurements on Au-lipid-Hg junctions have been made. The conductivity of thin films is generally higher than that of thick films. However, for thick films, the current-voltage data do not seem to be very sensitive to thickness. Both temperature measurement and photoresponse measurement show that the activation energy or barrier height is roughly the same for thin and thick films. The experimental results point to the fact that Schottky emission is the dominant conduction mechanism. The reason that the thin films have higher conductivity is that they have a higher intrinsic electric field. A model is proposed after taking into account the possible disorders in the structure. Based on this model, space charge is shown to occur due to existence of localized centers.

From the experimental data, the energy difference between the band edge and Fermi level (ϕ_i) is 1.008 eV. If the Fermi level is situated at the center of the band, the band gap is then twice the value of ϕ_i or 2.016 eV. This suggests that the lipid is a wide band gap material, which is not unusual for molecular amorphous solids. The density of states around the Fermi level is estimated to be about 1.31×10^{18} cm^{-3} eV^{-1}. The corresponding value for amorphous chalcogenides is believed to range from 10^{18} to 10^{21} cm^{-3} eV^{-1} (29). Our value is on the low side, which indicates that it is unlikely to have a large amount of dangling bonds in the center of the gap in our material. Our results as well as the model may be helpful in providing the clues for the electronic conduction in biological membrane, which has been a subject of speculation (30).

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