Photoelectron microscopy of organic surfaces: The effect of substrate reflectivity

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(Received 26 September 1975)

Photoelectron measurements of thin organic films deposited on a metal substrate may contain information from deep within the sample, derived from reflected ultraviolet light. This effect depends on the reflectivity of the substrate, the sample thickness and optical absorption coefficient, and the photoelectron escape depth. Calculations are given for phthalocyanine as a specific example. Contrast reversal and apparent see-through effects resulting from reflection are predicted in overlapping thin films. Photoelectron micrographs of thin films and grid patterns of phthalocyanine show that the reflection model is essentially correct. This effect can be substantially reduced by using a nitrocellulose-coated carbon substrate.

PACS numbers: 07.80., 87.20., 79.60., 81.50.Q

INTRODUCTION

Recently a number of laboratories have begun to investigate organic and biological materials by surface physics techniques such as ultraviolet and x-ray photoelectron spectroscopy and photoelectron microscopy. In these experiments, the organic sample is placed on a metal surface, whereas in the classical experiments the metal surface itself is the sample. During the photoelectric experiments novel effects sometimes arise that may be caused by the metal substrate. An example from photoelectron microscopy is shown in Fig. 1. These micrographs of overlapping phthalocyanine layers, deposited on stainless steel, are formed by electrons photoejected from the sample, accelerated, and focused by electron optics to produce an image of the surface. They show two interesting features. Both micrographs give the appearance of seeing through the top layer, clearly delineating the regions of overlap. Second, the sense of contrast depends on the film thicknesses. In Fig. 1(a), the region of overlap, 400 Å thick, appears dark compared to the adjacent layers, 150 and 250 Å thick. In Fig. 1(b), the region of overlap (150 Å) appears bright compared to the adjacent layers (50 and 100 Å). Similar photoelectron micrographs, using considerably thicker overlapping sections of methacrylate, have been observed by Engel. In this paper we propose a mechanism for the observed thickness dependence, based on the effect of ultraviolet light reflected from the substrate, and suggest substrates for studying organic and biological surfaces that minimize this effect.

MATERIALS AND METHODS

The photoelectron microscope used in this experiment is an ultrahigh vacuum instrument described previously. In this instrument the sample is illuminated at normal incidence with ultraviolet light. Sample rods of polished stainless steel, 6.35 mm in diameter, were used in studying the effect of a reflecting substrate. Nonreflecting substrates were prepared by depositing a layer of carbon on one end of the rod by vacuum evaporation. Carbon film thicknesses were determined by optical absorption at 400 nm of a film simultaneously evaporated onto a glass microscope cover slip. The absorption coefficient of Coslett and Coslett was used for these measurements. To suppress photoemission from the carbon coating, a thin film of nitrocellulose was deposited over the carbon. The carbon-coated sample rods were placed in a Buchner funnel equipped with drainage hose and clamp and filled with enough distilled water to cover the rod end surface to a depth of approximately 1 cm. One drop of 1% nitrocellulose in acetic acid was placed on the water surface and the solvent allowed to evaporate. The water was slowly removed from the bottom of the funnel, allowing the nitrocellulose film to settle onto the end of the sample rod. The rods were air dried at room temperature. Nitrocellulose was carefully removed from the sides of the rod by wiping with a cotton swab dipped in acetone. Metal-free phthalocyanine (Eastman Kodak Co., Rochester, N.Y.) was purified, and thin films were vacuum evaporated as described previously. The grid patterns were formed by evaporating through a standard 200-mesh electron microscope copper grid and then...
removing the grid. Film thicknesses for phthalocyanine were also determined by optical absorption at 400 nm, using an absorption coefficient of 0.64×10^4 cm^(-1) as reported by Lechmann. The thickness measurements were made with a Varian Λ-scope interferometer. Phthalocyanine film thicknesses reported in this paper were measured at 250 °C. All photographic micrographs presented here, the wavelength of the incident light was 220 ± 10 nm and the exposure time was 6 sec. The micrographs were recorded from the image intensifier on Kodak Tri-X emulsion and developed for 3 min in full strength Kodak D-X developer at 68 °F (20 °C). All samples were examined at room temperature in the photoelectro microscope.

CALCULATION OF THE REFLECTIVITY EFFECT

The following model is based on normally incident light penetrating an optically thin sample, reflecting from the substrate, and returning to the sample surface. Reflection of the returning wave at the sample surface is neglected. Light reflected from the substrate can carry information from deep within the sample relative to the photoelectron escape depth corresponding to variations in the optical properties of the sample. The surface layers receive equal incident light, but the superposition of incident and reflected light, in general, results in different intensities for different areas of the sample, with corresponding variations in photoemission. This is depicted in Fig. 2. We calculate the photocurrent observed from a phthalocyanine film of thickness D deposited on a substrate with a uniform film thickness profile, having maxima approximately at the antinodes of the standing-wave pattern in the sample, i.e., where the incident and reflected waves are in phase. The positions of the maxima depend on the wavelength of the light in the medium and also on the phase shift 0 occurring on reflection. When maximum observed photoemission occurs, there is a uv intensity maximum near the sample surface. Contrast reversals can arise from changes in either wavelength or sample thickness.

The reflection effect can strongly alter the observed photoemission, enhancing it by a factor of as much as 4 or reducing it to nearly zero. The effects are most prominent when the reflection coefficient is near unity and the absorption coefficient a is small compared with the wave number k. The curve for phthalocyanine in Fig. 3 shows that the photocurrent at maximum is greater by a factor of 4 or 5 for a reflecting substrate. This curve was explained in terms of standing light waves in the dielectric. Wegman reported interference effects in photoelectron micrographs of thin semiconductor films; he ascribed them to standing wave combinations with a photoelectron interference effect also evident in the grid patterns of Fig. 4. The film thicknesses are identical to those of Fig. 1, but in this case square patches of phthalocyanine were prepared first and then partially covered with uniform layers of phthalocyanine. The uncovered square patches of phthalocyanine are bright compared to the stainless-steel substrate. The grid pattern in the lower half of Fig. 4 corresponds to the phthalocyanine that has reversed contrast. In Fig. 4(b), there is no contrast reversal but there is an illusion of seeing through the 50-Å overlayers. These effects are all predicted by the above calculations and are consistent with the uniform film data of Fig. 1.

EXPERIMENTAL RESULTS AND DISCUSSION

Two sample geometries, uniform films and grid patterns of phthalocyanine, were examined. Typical results are shown in Figs. 1 and 4, respectively. The photocurrent micrographs of Fig. 1 are in qualitative agreement with the reflection calculations for the known value of k, 15 Å. In Fig. 1(a), the overlapping phthalocyanine film thicknesses are greater than Dmax. Thinner regions are thus predicted to photoemit less than thinner regions. This is the observed result, since the overlap region appears darker in Fig. 1(a). In Fig. 1(b), the overlapping film thickness is less than Dmax. In this case, the thicker overlap region appears brighter than the two thin films, in agreement with the calculations. The reflection effect is also evident in the grid patterns of Fig. 4. The film thicknesses are identical to those of Fig. 1, but in this case square patches of phthalocyanine were prepared first and then partially covered with uniform layers of phthalocyanine. The uncovered square patches of phthalocyanine are bright compared to the stainless-steel substrate. The grid pattern in the lower half of Fig. 4 corresponds to the phthalocyanine that has reversed contrast. In Fig. 4(b), there is no contrast reversal but there is an illusion of seeing through the 50-Å overlayers. These effects are all predicted by the above calculations and are consistent with the uniform film data of Fig. 1.
FIG. 5. (a) Overlapping layers of phthalocyanine on carbon-nitrocellulose substrate. Film thicknesses 100 Å followed by 250 Å. (b) Overlapping layers of phthalocyanine on carbon-nitrocellulose substrate. Film thicknesses 100 Å followed by 150 Å.

The authors wish to thank George H. Leech and Dr. W. Engel, Dr. M. Yago, and Dr. L. Wegmann for useful discussions and Keith F. Kongslie for expert technical assistance. This investigation was supported by a U.S. Public Health Service Research Grant from the National Cancer Institute.

ACKNOWLEDGMENTS

The wavelength of incident light. The above calculations can be applied to these systems quantitatively. Substrate reflection also helps to explain the data on overlapping sections of methyl methacrylate reported by Engel.

Besides photoelectron microscopy, the substrate reflection effect can alter uv photoelectron spectroscopy data and, at high angles of incidence, x-ray photoelectron spectroscopy data. It has not to our knowledge been taken into account in the photoelectron spectroscopy literature. However, it could be significant in quantitative measurements, particularly since substrate reflectivity varies with wavelength of incident light. In all of these experimental approaches it is desirable to be able to minimize the reflection effect. This can be accomplished by using either a transparent substrate or an absorbing substrate. The sample substrate must also exhibit some degree of electrical and thermal conductivity. We suggest for photoelectric studies of organic and biological surfaces an absorbing substrate. The sample substrate must also exhibit some degree of electrical and thermal conductivity. We suggest for photoelectric studies of organic and biological surfaces an absorbing substrate.

The carbon films thicker than 260 Å will, of course, reduce the reflection effect even further.