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distribution of spin density in metallic gadolinium agrees well with that calculated for the trivalent ion is not supported by this investigation. We believe the discrepancy is due to the inherently smaller precision of the unpolarized-beam method compared to the polarized-beam techniques, to the large number of parameters which they required for the reduction of their data, and to the high absorption in their specimen.

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Attenuation of Low-Energy Electrons by Solids: Results from X-Ray Photoelectron Spectroscopy*

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The scattering half-thickness for electrons has been experimentally determined to be $\approx 0.25 \mu\text{g}/\text{cm}^2$ ($\approx 13 \text{ \AA}$ carbon) for 1169-eV electrons and $\approx 0.21 \mu\text{g}/\text{cm}^2$ ($\approx 10 \text{ \AA}$ carbon) for 920-eV electrons. The corresponding mass-scattering coefficients are 2.75 ± 0.19 and $3.32 \pm 0.37 \text{ cm}^2/\mu\text{g}$. Other useful and related attenuation parameters are defined and calculated. These results were obtained from measurements of the attenuation by thin carbon films (5-60 \AA) of monoenergetic photoelectrons originating from gold substrates irradiated with Mg K_α x rays, and also from measurements of the concomitant increase in carbon photoelectron intensity. Scattering of electrons in the energy range about 1 keV is greater than has generally been indicated.

INTRODUCTION

The attenuation of low-energy electrons ($\approx 1000 \text{ eV}$) has become increasingly important because of

the growing use of high-resolution x-ray photoelectron spectroscopy for investigations in solid-state physics and chemistry.¹ While it is clear that x-ray photoelectron spectroscopy yields in-

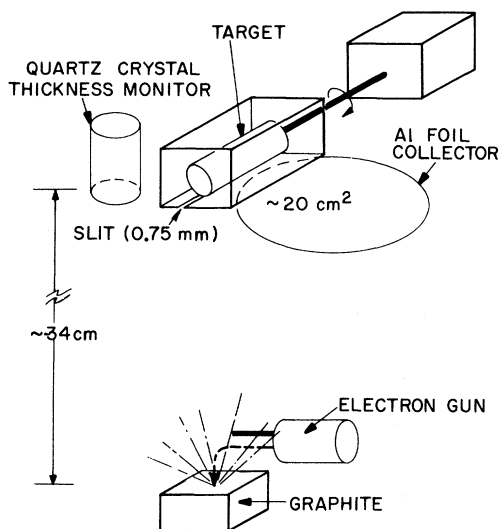


FIG. 1. Arrangement for vacuum deposition of thin carbon films onto gold cylinders. Enclosure around cylinder and a plate on the back of the foil collector prevented unwanted deposition of scattered carbon.

formation primarily about regions in and near the surface, little is known about low-energy-electron range parameters in solids, and such results as

are available do not appear to be in accord with one another.² For example, results³⁻⁶ with 5-50-eV electrons indicate that their mean free path lies between about 4 and 50 Å of Al; yet, essentially this same parameter for approximately 1000-eV electrons has been reported to be about 100^7 and 50 Å^8 for stearic acid derivatives. We have extrapolated data from higher electron energies⁹ and we obtain a value of about $0.75 \mu\text{g}/\text{cm}^2$ ($\approx 40 \text{ Å}$ carbon) for the mean range of 1000-eV electrons; however, such extrapolations are known to be unreliable.

In view of this uncertainty about the attenuation of low-energy electrons in solids, we have measured the relative intensities of monoenergetic electrons from characteristic photoelectron peaks of a gold substrate as a function of the thickness of carbon film deposited onto the gold. We have measured also the intensity of a photoelectron peak from the carbon as a function of film thickness.

EXPERIMENTAL PROCEDURE

Gold (99.99% pure) was chosen as the substrate because it is chemically stable and provides several strong photoelectron peaks in the desired energy range. The gold was evaporated in relatively thick layers ($125 \mu\text{g}/\text{cm}^2$) onto 1.1-cm-diam aluminum cylinders. Intensities of gold photoelectron peaks from substrates thus prepared remained substan-

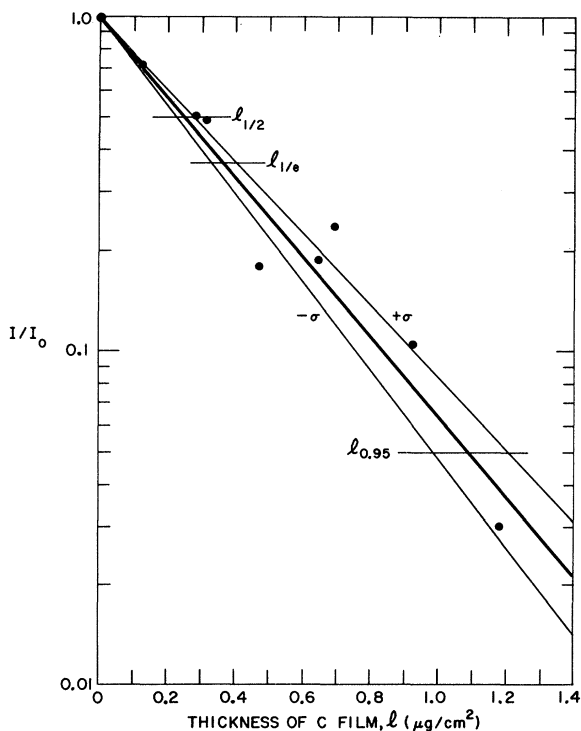


FIG. 2. Attenuation of Au $4f$ photoelectron peak by carbon films. Data for the $\frac{7}{2}-\frac{5}{2}$ doublet have been averaged. The heavy line represents a least-squares fit to the experimental points, and the σ lines show standard deviations.

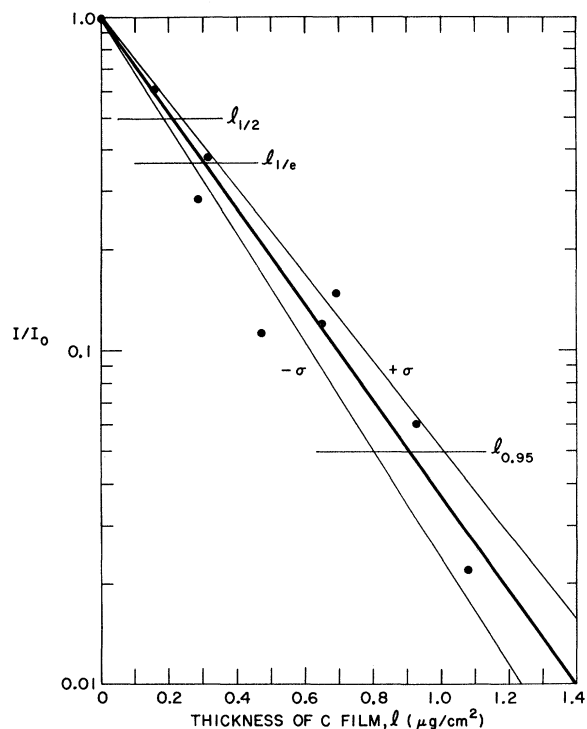


FIG. 3. Attenuation of Au $4d_{5/2}$ photoelectron peak by carbon films. See caption of Fig. 2 for details.

TABLE I. Electron transmission I/I_0 as a function of effective film thickness l .^{a,b}

Effective film thickness ($\mu\text{g}/\text{cm}^2$)	KE = 1171 eV (Au $4f_{7/2}$)		KE = 1167 eV (Au $4f_{5/2}$)		KE = 920 eV (Au $4d_{5/2}$)	
	Peak intensity I (counts/sec)	Transmission I/I_0	Peak intensity I (counts/sec)	Transmission I/I_0	Peak intensity I (counts/sec)	Transmission I/I_0
0	54 723 \pm 1000(av)	1.00 ^c	40 747 \pm 730(av)	1.00 ^c	15 054 \pm 350(av)	1.00 ^c
0.126	38 955 \pm 800	0.712 \pm 0.020	29 129 \pm 580	0.715 \pm 0.019	9 188 \pm 260	0.610 \pm 0.022
0.283	28 000 \pm 560	0.512 \pm 0.014	20 385 \pm 400	0.500 \pm 0.013	4 292 \pm 160	0.285 \pm 0.013
0.313	27 417 \pm 550	0.501 \pm 0.014	19 680 \pm 400	0.483 \pm 0.013	5 719 \pm 215	0.380 \pm 0.017
0.472	9 888 \pm 200	0.181 \pm 0.005	7 214 \pm 160	0.177 \pm 0.005	1 701 \pm 65	0.113 \pm 0.005
0.646	10 242 \pm 210	0.187 \pm 0.005	7 614 \pm 170	0.187 \pm 0.005	1 816 \pm 70	0.121 \pm 0.005
0.690	13 190 \pm 280	0.241 \pm 0.007	9 431 \pm 230	0.231 \pm 0.007	2 226 \pm 90	0.148 \pm 0.007
0.921	5 948 \pm 130	0.109 \pm 0.003	4 129 \pm 100	0.101 \pm 0.003	913 \pm 50	0.061 \pm 0.004
1.18	1 687 \pm 55	0.031 \pm 0.001	1 166 \pm 40	0.029 \pm 0.001	312 \pm 25	0.021 \pm 0.002

^aEffective film thickness equals actual film thickness times $\sqrt{2}$ (see text).

^bThe uncertainties are standard deviations.
^cDefinition.

tially constant over long periods of time. Carbon was chosen as the absorber because its low vapor pressure suggested that it would have little tendency to form islands in thin films. Islanding, commonly observed in thin metallic deposits,¹⁰ would lead to erroneously small values for scattering coefficients and correspondingly high range parameters.

Because of the difficulty of direct deposition of known thicknesses of carbon in the desired range (5–60 Å), a 0.075-mm slit was interposed between the shielded rotating (\approx 3000-rpm) substrate and the source of carbon. The carbon was evaporated by heating with an electron gun, and a quartz-crystal thickness monitor was used to estimate the rate of deposition and, roughly, the final film thickness. Graphite, 99.95% pure, was used for film preparation, and, before use, it was heated to 1450 °C in a vacuum induction furnace to eliminate the possibility of preferential evaporation of impurities. An aluminum foil (area = 20.25 cm²), mounted immediately adjacent to the slit (Fig. 1), was analyzed for carbon after each evaporation to determine the film thickness. Because of the large ratio between the areas of the slit and the aluminum foil and between the areas of the slit and the gold cylinder it was possible to measure reasonably accurately the thickness of the carbon films. Nevertheless, because the amounts of carbon deposited were extremely small, only 0.05–0.8 mg even on the aluminum foil, uncertainty in measurement of the carbon thicknesses is the dominant source of error in these experiments.

The spectrometer used was a Varian IEE equipped with a magnesium anode ($K\alpha_{1,2}$ energy = 1254 eV) and sample temperature control. The x-ray power supply was operated at 9 ± 0.1 kV and 80 ± 0.5 mA, and variations in x-ray intensity were thus held to less than a few percent. Pressure within the spectrometer during measurements was $3\text{--}5 \times 10^{-7}$

Torr.

Samples were stored and transferred to the spectrometer in argon, but were necessarily exposed to the atmosphere at time of sample insertion for about thirty seconds. In spite of the brevity of these exposures it was found that adsorption of impurities was occurring even on the "pure" gold that was used as the reference sample. For example, it was found that the "pure" gold showed about 7000 counts/sec for carbon and 4000 counts/sec for oxygen at their 1s peaks. However, these values could be reduced to about 4500 and 500 counts/sec, respectively, by heating the sample in the spectrometer vacuum at 250 °C until the Au peaks reached intensity maxima and the C and O peaks reached intensity minima. Similar behavior was observed in preliminary studies of carbon-coated gold, and measurements of all samples, including the periodically repeated measurements of the reference, were made with the heat treatment

TABLE II. Electron emission I'' from carbon as a function of effective carbon file thickness l .^a (C 1s electrons.)

Effective film thickness l ($\mu\text{g}/\text{cm}^2$)	I'' (counts/sec)
0	4 593 \pm 105 ^b (av)
0.126	8 580 \pm 400
0.283	13 148 \pm 665
0.313	12 228 \pm 450
0.472	15 768 \pm 685
0.646	15 694 \pm 650
0.690	14 774 \pm 490
0.921	15 666 \pm 610
1.18	16 956 \pm 700

^aEffective film thickness equals actual film thickness times $\sqrt{2}$ (see text).

^bThe uncertainties are standard deviations.

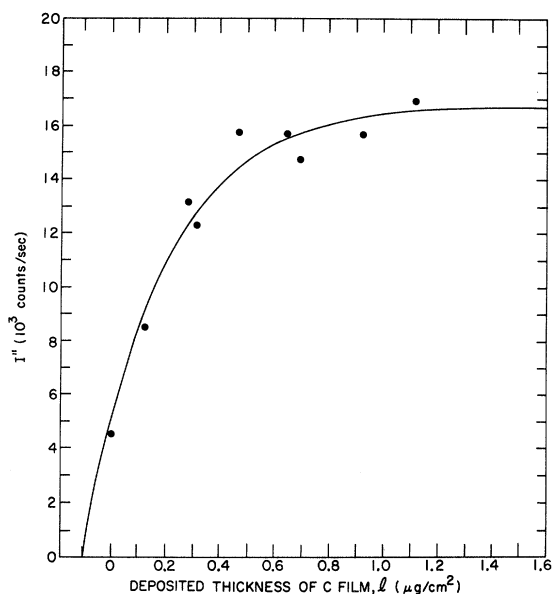


FIG. 4. Growth of intensity of the carbon 1s photoelectron peak with increasing thickness of carbon film deposited. Points are from experiment, and the line is fitted from a relation given in the text, where the nonzero abscissa intercept also is discussed.

at 250 °C. To reach constant peak intensities the heating times required ranged from two to three hours for the reference up to 24 hours for samples with the thickest carbon films; for the latter the transmission of Au electrons was increased as much as twofold. It is the final time-independent peak intensities which were used to calculate the range parameters reported here.

Electrons of four different kinetic energies were used: Au $4d_{5/2}$, 920 eV; C 1s, 970 eV; Au $4f_{5/2}$, 1167 eV; and Au $4f_{7/2}$, 1171 eV. Attenuation of the exciting x rays is negligible in depths from which electrons are detectable.¹¹ In the Varian instrument, electrons accepted by the analyzer emerge at an angle of 45° to the sample cylinder axis; therefore, the factor $\sqrt{2}$ has been applied to the measured carbon film thicknesses in order to obtain actual distances traversed through the carbon

films by electrons from the gold substrate. This means, for example, that, although the half-thickness for the Au 4f electrons is reported as 13 Å of carbon, the corresponding thickness measured perpendicular to the surface is $(13/\sqrt{2})$ Å \approx 9 Å.

Because the probability of very small energy losses in electron scattering is negligible, any interaction of an electron removes it from the peak. Thus the shape of a characteristic photoelectron peak is independent of the attenuation,¹² and intensity was conveniently determined from measurement of the peak height above a smoothly drawn baseline fixed by points adjacent to the peak. Full widths at half-maximum were 1.6 V (Au 4f), 4.2 V (Au 4d), and 2.2 V (C 1s).

RESULTS AND DISCUSSION

The Au transmission data are plotted in Figs. 2 and 3, and they are summarized in Table I. In Fig. 2, data for the two narrowly separated Au 4f lines have been averaged and assigned the electron energy 1169 eV. The attenuation of a low-energy electron peak may be expressed as

$$\ln I/I_0 = -\mu l,$$

in which I is the intensity of an Au peak in sample, I_0 is the intensity of an Au peak in reference, μ is the mass-scattering coefficient, and l is the thickness of the carbon film. In Table I, μ and l are expressed in units of mass and area in order to make the results relatively insensitive to atomic number and density. For convenience, some results are given also in Å of carbon, with the density taken to be 2.0 g/cm³. The Au transmission data were analyzed by determining the least-squares lines of regression, shown in Figs. 2 and 3; in these analyses the observation that errors in l are dominant over errors in I/I_0 was taken into account.

Emission data for C 1s electrons (energy 970 eV) are summarized in Table II and plotted in Fig. 4. The equation representing these results is

$$I'' = (I'/\mu)(1 - e^{-\mu l}), \quad (1)$$

in which I'' is the C 1s intensity and $I' = \lim_{l \rightarrow 0} I''/l$. Values for the best fit of the data are I'/μ

TABLE III. Summary of electron range parameters.

Electron energy (eV)	$(\mu\text{g}/\text{cm}^2)$	$l_{1/2}$ (Å)	$(\mu\text{g}/\text{cm}^2)$	λ (Å)	$(\mu\text{g}/\text{cm}^2)$	$l_{0.95}$ (Å)	$(\mu\text{g}/\text{cm}^2)$	$l_{0.99}$ (Å)	μ (cm ² /μg)
920 ^a	0.21 ± 0.02 ^b	10 ^c	0.30 ± 0.03	15	0.90 ± 0.10	45	1.39 ± 0.16	70	3.32 ± 0.37
970 ^d	0.20 ± 0.03	10	0.29 ± 0.05	15	0.86 ± 0.14	43	1.32 ± 0.22	66	3.48 ± 0.57
1169 ^a	0.25 ± 0.03	13	0.36 ± 0.04	18	1.09 ± 0.11	55	1.67 ± 0.17	84	2.75 ± 0.28

^aGold transmission data. The 1169 entries are an average of the 1167- and 1171-eV data.

^bThe uncertainties are standard deviations.

^cThickness in Å are calculated from surface densities with the assumption $\rho_{\text{carbon}} = 2.0$ g/cm³.

^dCarbon emission data.

= 16 800 counts/sec (the limit of intensity for infinite thickness) and $\mu = 3.48 \text{ cm}^2/\mu\text{g}$ (Table III). These results (Fig. 4) indicate that the reference has the equivalent of about $0.1 \mu\text{g}/\text{cm}^2$ C impurity on its surface; however, the Au transmission results are unaffected because they are calculated on the basis of additional thickness of carbon deposited.

In Table III the results are summarized in terms of μ and four convenient parameters defined as follows:

parameter	I/I_0
half-thickness $l_{1/2}$	0.5
mean free path λ	$1/e$
95% range $l_{0.95}$	0.05
99% range $l_{0.99}$	0.01

Because the uncertainties in the μ values of Table III reflect mainly the uncertainties in the film thicknesses, they are correlated. A ratio of μ values thus has a relatively small uncertainty which depends mainly on counting rate variations; for example, $\mu_{1169}/\mu_{920} = 0.83 \pm 0.02$.

The range parameters reported here tend to be lower than the few approximate data previously available.³⁻⁸ It is worth pointing out that any non-uniformity of thin-absorber deposits, such as can be caused by clumping or islanding, would produce erroneously large ranges.

Note added in proof. Two publications about attenuation of low-energy electrons by solids have recently come to our attention. Palmberg and

Rhodin [J. Appl. Phys. **39**, 2425 (1968)] found that the mean scattering depth λ for 950-eV electrons is not more than 3-4 monolayers of Au, about 8 \AA or $1.5 \mu\text{g}/\text{cm}^2$. On the other hand, for electrons of roughly the same energy, 1.2 keV, a considerably larger depth of $22 \pm 4 \text{ \AA}$ of Au has been reported by Baer, Heden, Hedman, Klasson, and Nordling [Solid State Commun. **8**, 1479 (1970)]. Both of these values for the mean scattering depth in Au are larger than the value $0.29 \pm 0.05 \mu\text{g}/\text{cm}^2$ that we find for 970-eV electrons in carbon. However, comparison of the Au and C values requires corrections for (a) the relative numbers of electrons per unit mass of C and Au energetically available for scattering at incident energy 0.97-1.2 keV, and (b) the relative scattering cross sections for the various electron shells in the two atoms. Although we have no estimate of this latter factor, correction for available number of scattering electrons would make the Au λ value, expressed in mass per unit area, about twice that for C.

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