There is also, of course, the possibility that the apparently constant hyperfine fields are a result of compensating effects between the crystal structure and the actual Fe moment in the compositions investigated.

The $(Fe_{0.77}Al_{0.23})_2O_3$ composition was investigated with the specific purpose of examining whether line broadening occurred as a result of local fluctuations in the hyperfine field due to different numbers of nearest Fe neighbors. This effect was observed in the FeAl system[36] and is largest in the case of the two outermost peaks. The Al ion was selected because of its nonmagnetic nature. Figure 7 shows the observed and calculated absorption peaks for $(Fe_{0.8}Al_{0.2})_2O_3$ as well as Fe_2O_3. Both curves were calculated with $\Gamma=0.30$ mm/sec and a peak ratio of 3:2:1. The function $y=(1+x^2/\Gamma^2)^{-1}$ was utilized in order to ensure proper behavior at large x. Noticeable line broadening was not observed.

[36] P. A. Flinn and S. L. Ruby, Phys. Rev. 124, 34 (1961).

This result is in accordance with the model that the hyperfine field observed by the Mössbauer measurements is proportional to the moment at a given temperature, and not to the component of the moment along the magnetic axis. The latter may be affected by local fluctuations caused by the number of Fe neighbors but the moment itself retains the proper value for Fe^{3+}. In the metallic Fe—Al system, on the other hand, the moment is dependent upon the distribution amongst the nearest metal neighbors.

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Optical Spectrum of the Semiconductor Surface States from Frustrated Total Internal Reflections

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Through the use of multiple internal reflection and a modulation of the charge in the surface via the field effect, sufficient sensitivity is obtained to observe absorption of infrared radiation resulting from transitions involving the semiconductor surface states. This offers the possibility of obtaining the optical spectra and thus some rather direct information about the surface states. The principal other mechanism which contributes to the signal in this experiment is the free-carrier absorption arising from a modulation of the free-carrier density in the semiconductor space-charge region. The results of some observations on a silicon surface are discussed.

INTRODUCTION AND TECHNIQUE

INTERNAL reflection of radiation from a semiconductor surface is less than total because of absorption at the surface. A measure of this absorption can be used to monitor the free-carrier density in the semiconductor space-charge region[1] and to obtain the spectra of foreign molecules chemisorbed on the surface.[2] The purpose of this paper is to present evidence that absorption resulting from optical transitions involving the surface states can also be detected, hence the spectrum of the semiconductor surface states can be obtained from an analysis of internally reflected radiation. The importance of being able to obtain some very direct information regarding the surface states, as might be done from the optical spectrum, can be appreciated when it is recalled that in analyzing the results obtained from field effect and conductivity measurements, which have been so widely used to date, the number of parameters are increased and adjusted until agreement with experiment is obtained.

Because of the low density of the surface states,[3] manyfold increase of sensitivity must be obtained over conventional infrared spectroscopy in order to observe them. Figure 1(a) is a schematic diagram of the technique used in the present experiment where the required gain in sensitivity comes from two sources. Firstly, the use of multiple internal reflections serves to give a direct increase in signal strength.[2] Secondly, by modulating the population in the surface states through the use of an external alternating electric field, instead of chopping the infrared, it is possible to amplify only the change in the infrared intensity resulting from a change

[1] N. J. Harrick, J. Phys. Chem. Solids 8, 106 (1958).
[2] N. J. Harrick, Phys. Rev. Letters 4, 224 (1960).

[3] *Proceedings of the Second Conference on Semiconductor Surfaces* (Pergamon Press, New York, 1960).

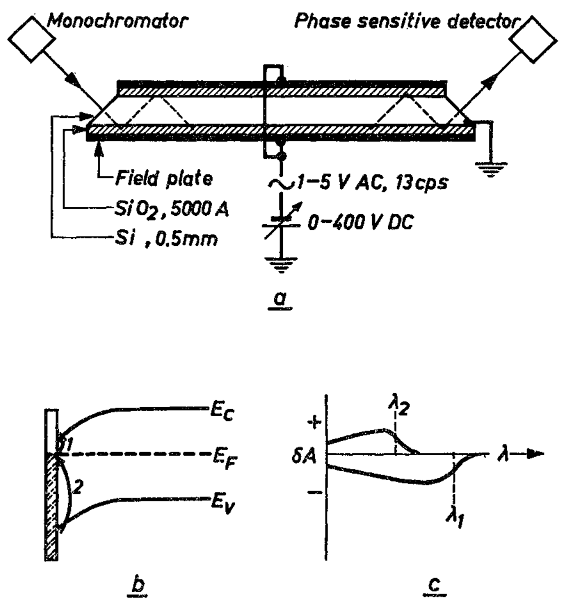

FIG. 1. Schematic diagram showing the principles involved in the setup used to observe the optical spectrum of the semiconductor surface states.

in the absorption by the surface. With these techniques we have measured reflectivity changes of less than one part per million and have gotten satisfactory measurements with a modulation of carriers in the surface corresponding to only about 2×10^{10} electronic charges per cm^2 which is a gain of about 10^4 over conventional infrared spectroscopy.

The samples used for the experiments to date, shown in Fig. 1(a), were made from silicon and had a thickness of 0.5 mm and lengths up to 5 cm. Our samples were cut so that the angle of incidence was 45° because this is a convenient angle to work with and also gives us the largest aperture for a given thickness.[4] In some instances, 20% of the incident infrared power was collected at the detector after 100 internal reflections when the expected power out was less than 50% because of reflection losses at the entrance and exit faces.

The dielectric separating the semiconductor and field plate should be non-absorbing and bonded to the surface; otherwise spurious signals may arise because the reflected radiation actually penetrates into the rarer medium. Silicion dioxide grown on the silicon surface is satisfactory in this respect since it is transparent up to a wavelength of nine microns[5] and has a high dielectric breakdown. However, when metallic contact was made to the oxide, the leakage current was found to be too high. Hence we either used another dielectric in place of or in addition to the oxide or replaced the metal field plate by the liquid N-methylacetamide with $0.04N$ potassium nitrate.[6] Fields as high as 10^7 v/cm were developed at the silicon surface with the aid of this electrolyte which served to anodize the silicon further, hence repair the oxide at the weak spots and/or block the current at these weak spots because of the rectification action. The importance of the use of high fields will become evident when it will be shown that with the aid of the high fields we were able to separate the two principal mechanisms contributing to the signals.

For the measurements shown in Fig. 3 the sample was n-type silicon of 1500 ohm-cm resistivity with an initially slightly n^+ surface and was 22 mm long (44 reflections). In the final step of preparation the surfaces were polished with diamond grit of one-micron diameter and were then thermally oxidized until an oxide film 5000 A thick was grown. The dc bias was always of one sign (sample positive) because only for this polarity can very low leakage currents be obtained when the liquid is used as the field plate. The modulation frequency of 13 cps eliminates the slow states in our measurements. The measurements shown were made with a modulation of 5 volts ac and a bias of 0 to 300 v dc. The capacity was measured as a function of bias so that the charge induced in the surface could be determined more accurately.

ANALYSIS

In this experiment one might expect the following four mechanisms to be involved: (a) optical transitions involving the semiconductor surface states; (b) free-carrier absorption in the semiconductor space-charge region; (c) field-assisted absorption; (d) change of index of refraction at the surface arising from the change of free-carrier density in the space-charge region. These four mechanisms will be discussed in order and it will be shown that in the analysis of the experimental results only the first two need to be considered.

(a) The optical transitions involving the surface states are shown schematically in Fig. 1(b). The intensity of the signals will be proportional to the density of surface states at the Fermi level. If electrons are taken out of the surface states via the modulating field, the changes in the absorption for transitions 1 and 2 should exhibit an increase and a decrease, respectively, over a wide wavelength range but terminating at wavelengths λ_1 and λ_2 as shown in Fig. 1(c). For surface states located at midgap the changes in the absorption due to these two transitions can compensate almost completely and little or no net change in absorption may be observed when the charge in the surface states is

[4] It should be realized, however, that by working at angles nearer to the critical angle, even though the aperture decreases, an increase in sensitivity can be obtained for two reasons. First, the number of internal reflections increases. Second, the electromagnetic field intensity at the surface increases, hence the absorption increases. [Cl. Schaefer and G. Gross, Ann. Physik **32**, 648 (1910).] This latter point can be appreciated by recalling that the penetration depth into the rarer medium increases as the critical angle is approached.

[5] J. R. Ligenza and W. G. Spitzer, *Proceedings of the Second Conference on Semiconductor Surfaces* (Pergamon Press, New York, 1960), p. 131.

[6] P. F. Schmidt and W. Michel, J. Electrochem. Soc. **104**, 230 (1957). A. Polotycki and E. Fuchs, Z. Naturforsch. **14a**, 271 (1959).

FIG. 2. Photograph of recorder tracings showing surface-state and free-carrier absorption for a silicon surface. A constant modulation potential of 25 volts ac was applied to the field plate to obtain these curves. The dc bias was changed in steps of 10 volts in the range from 10 to 70 volts and 60 to 110 volts for curves *a* and *b*, respectively, while for curves *c* the dc bias was changed in steps of 20 volts in the range from 110 to 230 volts. The amplifier gain was adjusted, where necessary, to normalize the curves at the longer wavelengths so that the relative changes of absorption at the shorter wavelengths might be compared more easily. The part of the signal whose character changes with bias is attributed to surface state absorption while the signal whose character is independent of bias is attributed to free carrier absorption in the semiconductor space-charge region.

changed. Because of the low density and of the probably localized character of the surface states, interstate transitions are considered unlikely. By adjusting the surface potential through the use of an external dc bias or by changing the gaseous ambient, the whole of the forbidden region can be searched for surface states.

(b) If the modulating field alters the free carrier density in the semiconductor space-charge region, a broad background of absorption will be observed characteristic of free carrier absorption. Most theories predict roughly a λ^2 dependence for this intraband absorption although variations from this do occur.[7] Deviations from a λ^2 dependence for holes are also found because of interband transitions which occur in Ge in the 2- to 5-micron region.[8] Such transitions are predicted for Si in the 20- to 30-micron region,[8] but they have not yet been found. For electrons in Si there appears to be a weak absorption band attributed to an interband transition at two microns[9] which is superimposed on a broad λ^2 absorption. The maximum absorption cross section of this band is only about 10^{-17} cm^2. In addition to these deviations, it should be emphasized that absorption by free carriers in the space-charge region may differ from that in the bulk[10] just as the mobility of carriers in the space-charge region differs from that in the bulk. The present type of experiment offers an excellent possibility for studying the deviations of the type discussed above since with the proper bias only the hole or electron density in the surface can be modulated. The absorption change due to the free

[7] H. J. G. Meyer, Phys. Rev. **112**, 298 (1958).
[8] A. H. Kahn, Phys. Rev. **97**, 1647 (1955).
[9] W. Spitzer and H. Y. Fan, Phys. Rev. **108**, 268 (1957). W. Huldt and T. Staflin, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), p. 385.
[10] N. J. Harrick, J. Phys. Chem. Solids **14**, 60 (1960).

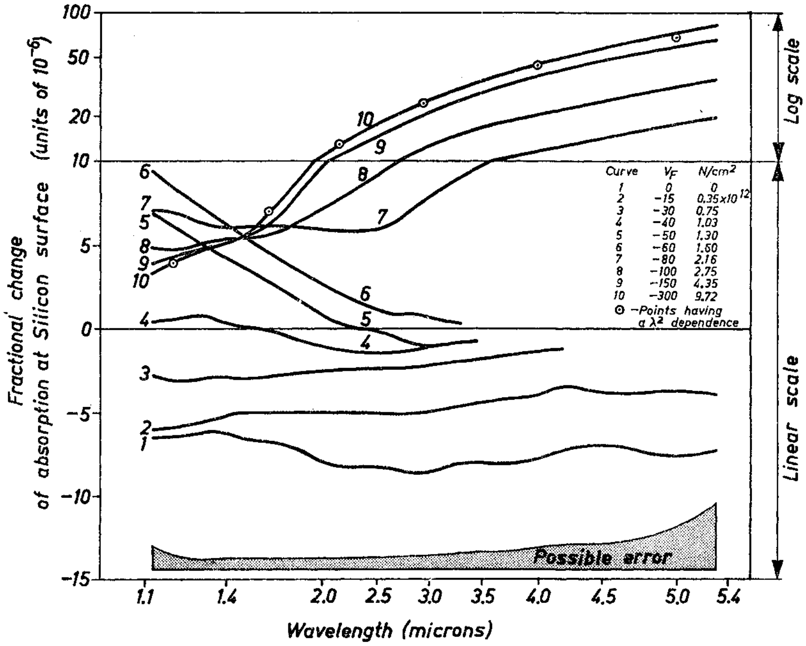

FIG. 3. Change of the fractional absorption of an oxidized silicon surface resulting from an application of 5 volts ac to the field plate for various values of positive charge in the surface. The phase of the detector is such that the signals shown result from the subtraction of electrons (about 10^{11} charge cm^2 at zero bias) from the surface. The charge induced in the surface, which is controlled by the dc bias and shown in the table, has been calculated taking into consideration the change (measured) in the capacity of the space-charge region.

carriers in the space-charge region will be positive or negative according to whether carriers are added to or subtracted from the surface. Near the conductivity minimum both holes and electrons will contribute to the signal and an increase of absorption of one will tend to compensate the decrease of absorption of the other.[1] From a measure of the signal due to free carrier absorption at long wavelengths, where it should predominate because of the strong wavelength dependence, an independent determination can be made of the surface potential if the absorption coefficients of electrons and holes in the space-charge region are known.[1] Furthermore, the amount of charge that goes into the space-charge region can be monitored in this way.

(c) We cannot with certainty separate the contribution to our absorption signals arising from field-assisted absorption.[11] This effect, however, will be significant only near the fundamental band to band absorption edge and hence we will not discuss it further at this time. We have observed it in photoconductivity measurements. Some measurements for silicon have recently been reported by Keldyš *et al.*[11]

(d) The added free carriers in the space-charge region tend to lower the index of refraction near the surface at these wavelengths[12] and thus cannot alter the net reflectivity which is already total. They can, however, serve to effectively shift the plane of reflection some distance inside the actual surface. (This phenomenon reminds one of the reflection of radio waves from the ionosphere.) From a consideration of the carrier distribution in the space-charge region determined from the shape and extent of the space-charge region,[13] our estimate is that this shift is certainly less than 50 A for the wavelength range investigated even for the case that the surface barrier is changed from 0 to $20kT/q$ for intrinsic silicon. Since this distance is small compared to the wavelength used and also small compared to the depth of penetration of the radiation in the rarer medium (>1000 A), this phenomenon cannot have a significant effect on the surface-state or free-carrier absorption.[14]

RESULTS AND DISCUSSION

Evidence for mechanisms (a) and (b), viz., surface state and free carrier absorption, is given in Figs. 2–4 which represent the observed signal for one and the same surface but for different values of total charge in the surface. It should be recalled that we are measuring only changes of absorption as the carrier concentration

[11] W. Franz, Z. Naturforsch. **13a**, 484 (1958). L. W. Keldysch, Soviet Phys.—JETP **7**, 788 (1958). K. W. Böer, Z. Physik **155**, 184 (1959). R. Williams, Phys. Rev. **117**, 1487 (1960). L. V. Keldyš, V. S. Vavilov, and K. I. Bricin, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), p. 824.

[12] The contribution of free carriers to the index of refraction is discussed, for example, by W. G. Spitzer and H. Y. Fan, Phys. Rev. **106**, 882 (1957).

[13] C. G. B. Garrett and W. H. Brattain, Phys. Rev. **99**, 376 (1955).

[14] This phenomenon can, however, be observed as a signal of opposite sign to the free carrier absorption if the rarer medium (dielectric) is strongly absorbing; i.e., a modulation of the depth of penetration in a strongly absorbing dielectric will give rise to such a signal. We have demonstrated this effect by making measurements at wavelengths corresponding to absorption bands in the rarer medium. For the absorption band in SiO_2 occurring at 9.2 μ[5] the signal arising from this effect was found to be less than that due to free carrier absorption. As pointed out earlier, it is advisable to choose a nonabsorbing dielectric and thus eliminate the major signal arising from this effect. We hope, with the aid of quantitative measurements, to discuss this phenomenon more precisely in the future.

in the surface is changed. Since phase-sensitive detection is employed, we elect to discuss our signals arising from the modulating field in terms of subtraction of electrons from the surface or equivalently in terms of addition of holes to the surface. Thus electrons subtracted from the space-charge region of an n-type surface will lead to an increase of transmission or a decrease of absorption, while electrons subtracted from (or holes added to) the space-charge region of a p-type surface will lead to a decrease of transmission or an increase in absorption. Some ambiguity arises near the conductivity minimum, just as in conductivity measurements, since the absorption coefficient for holes is greater than that for electrons.

In Fig. 2 we give an example of some recorder tracings where the curves have been normalized at the longer wavelengths by adjusting the amplifier gain, where necessary, so that the surface-state and free-carrier absorption might be more readily distinguished. These curves have not been adjusted for a variation with wavelength of the infrared intensity and the apparent absorption bands reflect a low intensity of infrared at these wavelengths due to atmospheric water and carbon dioxide. The negative signals indicate an n-type surface while the positive signals indicate a p-type surface as discussed above. To recognize any free carrier absorption we look for a signal independent of bias. This we see only at the longer wavelengths in curves 2(a), over a greater wavelength range for curves 2(b), and over the entire wavelength range for the last four curves of 2(c). It will be shown in Fig. 3 that this asymptotic curve follows a λ^2 dependence closely which is characteristic of free-carrier absorption. The other component of the signal, which we see changes both in magnitude and character as the bias is changed, is attributed to surface-state absorption. We note the decrease in surface-state absorption with increasing bias for curves 2(b) and 2(c). For the curves 2(a), where there is more surface state activity, there is a relative decrease in the signal at the shorter wavelengths and a relative increase at the intermediate wavelengths as the charge in the surface is increased. The change in the character of the curves with bias can be accounted for in terms of the relative predominance of transition 1 or transition 2 of Fig. 1(b) and the expected motion of the absorption edge as the surface potential is changed; thus we observe the sort of activity expected to result from surface state absorption.

If we take curves of the type shown in Fig. 2 and adjust them for the change with wavelength of infrared intensity emitted by the source, we obtain curves similar to those shown in Fig. 3 where for clarity only a few selected curves have been plotted. It should be noted that the modulation potential is only 5 volts ac for these curves compared to 25 v ac for the demonstration curves of Fig. 2. The signals observed are of the magnitude expected assuming an absorption cross section for infrared radiation of the order of 10^{-16} cm^2. The measurements show that for low dc biases most of the induced charge is absorbed by the semiconductor sur-

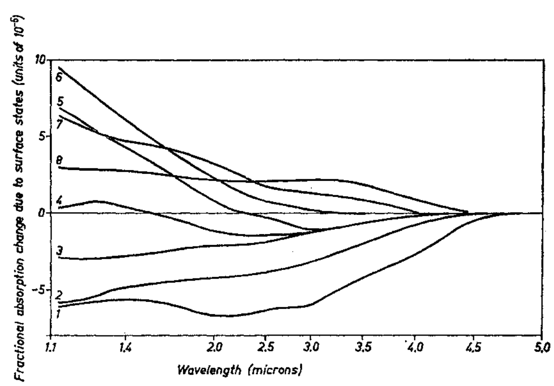

FIG. 4. The change of surface state absorption for various values of positive charge in the silicon surface. These curves are obtained from corresponding ones in Fig. 3 by subtracting an appropriate λ^2 component.

face states, while for high dc biases most of the charge goes into the semiconductor space-charge region. Initially a decrease in absorption is observed at all wavelengths when electrons are subtracted from the surface. From this we conclude that transition 1 of Fig. 1(b) is the dominating process and that the surface is slightly n^+. As the bias voltage is applied (field plate negative) and electrons are taken out of the surface, the signals due to transition 1 decrease, as would be expected. For flat band condition, curve 4, positive signals are observed for short wavelength and negative for longer wavelengths. The small magnitude of the signals indicates a high degree of compensation for transitions 1 and 2 of Fig. 1(b). When the surface becomes p-type, the positive signals corresponding to transition 2 of Fig. 1(b) predominate. The surface type was checked independently for all biases by measuring the surface photo voltage and was found to change type at just over forty volts as would be expected from the curves of Fig. 3. As the dc bias is further increased, the signals tend to increase at the longer wavelengths and decrease at the shorter wavelengths. Eventually the signals become almost independent of bias as may be noted by the small change in the signal between curves 9 and 10 of Fig. 3 even though the bias is changed from 150 to 300 v. This broad background absorption, independent of bias, is just what we would expect if the induced charge is all going into the space-charge region. Convincing support of the conclusion that for large biases the induced charge is going entirely into the space-charge region is given by the points (circles in Fig. 3) which follow curve 10 rather closely. One point was adjusted to curve 10 while the others were calculated assuming a λ^2 dependence. Such a λ^2 dependence for absorption of infrared radiation by holes in silicon has been reported by Fan.[15] Our measurements thus indicate that the density of surface states decreases uniformly from the middle of the forbidden region and few or no states are found near the top of the

[15] H. Y. Fan, *Report on Progress in Physics* (The Physical Society, London, 1956), p. 107.

valence band. No evidence was found for slow surface states, which is not unexpected for thermally oxidized silicon.[16]

We wish now to separate, for the curves in Fig. 3, the components of the signals arising from absorption by the carriers in the surface states and in the space-charge region. To do this we assume that because of the strong wavelength dependence for free-carrier absorption, the signals at the longest wavelengths measured arise chiefly from free-carrier absorption. Thus one of the components can be determined. There is obviously no difficulty about this for curves 7–10 where a large part if not all of the signal follows a λ^2 dependence and can be attributed to free hole absorption in the space-charge region. For curves 4–6 little or no correction is made for free-carrier absorption since the signals already resemble those to be expected from surface-state absorption and no λ^2 region can be identified. For curves 1–3, which correspond to a slightly *n*-type surface, any free-carrier absorption will be dominated by electron absorption. We do not know the exact magnitude for this correction since a λ^2 region has not been identified nor have we found any evidence for the weak absorption band at two microns. However, since a large part of free-electron absorption is expected to follow a λ^2 dependence,[9] we subtract a small component, the strength of which is determined by the signal at the longest wavelength measured. No correction is made for the possible existence of a weak band at two microns. There is a possibility that we have overcorrected for the free-carrier contribution for these three curves. If that is so, the absorption edges for these curves should appear at somewhat longer wavelengths than those indicated in Fig. 4.

After the free-carrier absorption has been subtracted from the curves of Fig. 3, in the manner indicated above, the signals shown in Fig. 4 remain which we attribute to absorption involving the surface states. We note that no signal appears for curves 9 and 10. Absorption edges do appear as predicted. They are not very sharp but they do move in the expected direction as the surface is driven from slightly *n* type to *p* type. The lack of sharpness of the absorption edges can be understood in terms of the distribution of states in the valence and conduction bands, the continuous distribution of surface states, the distribution in the population in the surface states expected at room temperature, and the mixture of signals arising from transitions to and from the surface states.

The above results indicate that for the surface studied, there is a large density ($\sim 10^{12}/cm^2$) of surface states near midgap with a decrease as the top edge of the valence band is approached. Similar results were observed for a 500-ohm—cm, *p*-type sample whose surface was treated in the same way. Our measurements on a freshly diamond-polished silicon surface revealed a broad absorption band, although we were unable to "bend the bands" with the dc bias and search a larger portion of the forbidden region.

[16] M. M. Atalla, E. Tannenbaum, and E. J. Scheibner, Bell System Tech. J. **38**, 749 (1959).

CONCLUSION

The results discussed above demonstrate that it is possible to observe directly absorption of radiation by the semiconductor surface states and thus to obtain the optical spectrum of the surface states. Other problems associated with this experiment must be studied. Absorption of radiation by the free carriers in the space-charge region must be measured so that a correction for this absorption can be properly taken into account, especially where deviations from a λ^2 absorption are expected. The present type of experiment enables one to make such studies for electrons as well as holes if an appropriate dielectric can be found which would permit one to apply large positive and negative fields at the surface. Such studies are automatically made in doing the present type of experiment as we have demonstrated here for a *p*-type silicon surface. Surfaces prepared in a different way must also be studied. Optically flat surfaces are not absolutely necessary but they are desirable. Electropolishing techniques do exist[17] by means of which surfaces can be etched optically flat so that the etched surface can be studied. Surfaces as grown (for example, dendritic crystals) may lend themselves to study in this way. In principle, the clean surface can be studied since ultra-high vacuum would serve as an excellent dielectric. Care must be exercised to maintain chemical uniformity for surfaces of such large areas. Finally, measurements at lower temperatures should also be considered in attempt to sharpen the absorption edges.

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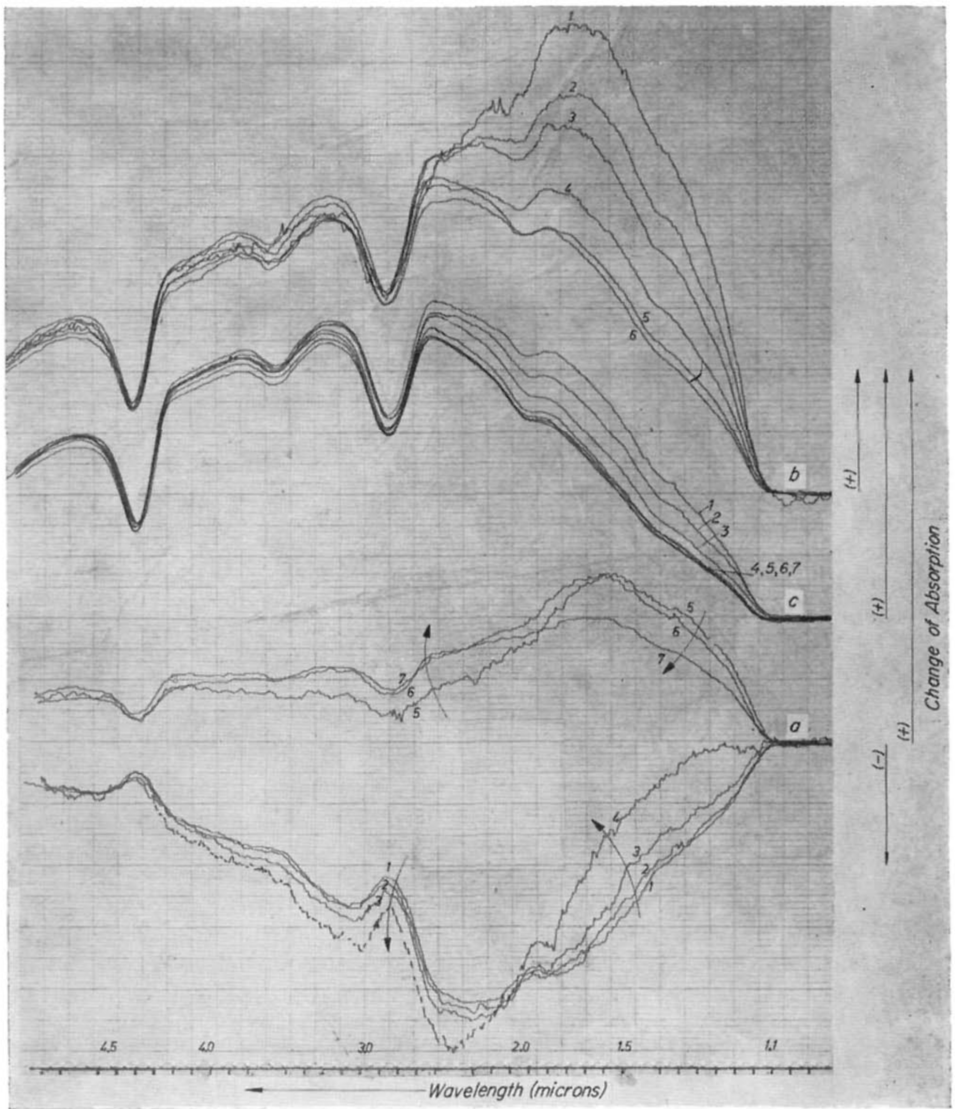
[17] D. L. Klein *et al.*, Bulletin of Indianapolis Meeting of the Electrochemical Society, April, 1961 (unpublished).



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