Ellipsometry for the Study of Gold Surfaces

ADSORBED FILM CHARACTERISATION AT THE MONOMOLECULAR LEVEL

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Ellipsometry is an elegant and sensitive method for the study of surface films. This article outlines the technique and describes an investigation of the adsorption of organic vapours on the faces of gold contacts in which it was essential to maintain experimental conditions as close as possible to those of actual works practice.

Recent work at the Sir John Cass School of Science and Technology has shown the effectiveness of ellipsometry as a technique for detecting and examining the characteristics of adsorbed organic films on metal surfaces. Ellipsometry utilises the changes which occur in a beam of monochromatic polarised light when it is reflected obliquely from the surface being examined. The sensitivity of the technique is very high and films ranging in thickness from monolayers to a few hundred Ångströms can be studied. The metal surface being examined is exposed at all times to the atmospheric conditions from which surface contamination has been derived and this is a considerable advantage. Thus the growth of surface layers can be followed as a function of time or of ambient vapour pressure, and the gradual thickening of the films can be determined from changes in the relative phase (Δ) and relative amplitude (ψ) of the component electric vectors of the light reflected from the specimen surface.

The applications of ellipsometry are being extended continuously to a wide variety of situations where surface films and structure, as well as optical properties, are of primary importance. The technique is well suited to the determination of optical constants, and since these in turn lead to information about the electronic structure of the material under investigation it will be no surprise that physicists have used it extensively – extending the wavelength region into the infra-red and ultra-violet. The optical constants are sensitive indicators of the visual appearance of a material, and the ellipsometric technique is rapidly approaching the point when it should be able to measure, or at least to say something, about surface quality with respect to colour and to finish.

It is, perhaps, in the study of surface layers and films that ellipsometry has been applied most widely and will make valuable contributions. Obviously, chemical and electrochemical processes have been studied. For example, the passivation of iron by nitric acid was used as one of the first models for applying ellipsometry to a "growing film" situation. Subsequently, not only passivation and anodisation have been investigated but electropolishing, tarnish reactions and electrodeposition have all received at least some attention A number of investigators have looked at gas/solid interfaces under conditions ranging from ultra-high vacuum to high pressure. These have included studies of thermal oxidation, vacuum pump oil contamination, catalysis, and, as in this study, vapour adsorption.

Since films and surface reactions have technological significance in fields as diverse as medicine and optical engineering, e.g. studies of blood coagulation in the first case and of evaporated dielectric films in the second, the general applicability and usefulness of ellipsometry has been well demonstrated.

The ellipsometer employed at Sir John Cass School of Science and Technology is a very high sensitivity automatic tracking instrument, which gives a continuous graphical and numerical read-out of the optical parameters. Figure 1 provides a general view of the experimental arrangements and Figure 2 illustrates diagrammatically the optical principles involved.

Organic Films on Gold Contacts

One investigation carried out with this instrument has concerned the identification of organic films formed on the working faces of gold contacts for use in sensitive circuits. Because of its inertness, gold does not encourage the growth of those organic polymer films which sometimes form on the surface of other noble metals. Gold contacts are therefore extensively employed for low voltage, low pressure applications, where contact resistance measurements provide a sensitive indication of the cleanliness of the

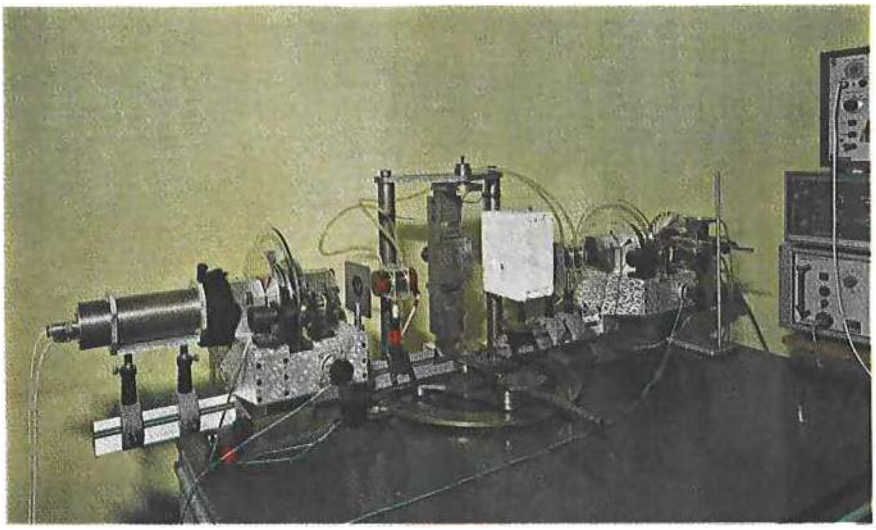

Fig. 1 The ellipsometer designed and built at the Sir John Cass School of Science and Technology. This is a high sensitivity automatic tracking instrument giving a continuous graphical and numeral read-out of the optical parameters characteristic of the structure and growth of surface films

contact surfaces. From such electrical measurements the presence of thin adsorbed layers of foreign materials at the contact surfaces can frequently be inferred, but these remain undetectable by normal methods of surface examination. This is because alternative methods of surface examination require high vacuum conditions for their satisfactory operation. This divorces the conditions of examination from those in which contamination occurred, with the result that adsorbed layers decompose or evaporate, leaving the source and nature of the contamination a continuing mystery.

During a series of experiments with gold and gold alloy contact materials, bottles containing a number of proprietary industrial working lubricants were opened in the laboratory a metre or so away from the clean specimen surface. Within a few seconds considerable changes in the phase angle Δ occurred, and the discontinuous build-up of phase angle as the vapours from the other lubricants met the specimen surface can be seen from Fig. 3.

Lubricant E (solid wool fat in trichloroethylene with soap additive), the vapour of which had an outstanding effect on phase angle, contained substantial quantities of trichloroethylene and the almost instantaneous adsorption of this compound on a clean gold surface is shown in Fig. 4. Attempts to remove these adsorbed layers by the use of liquid solvents such as acetone, alcohol or benzene usually resulted in surface changes which were even more severe than those caused by the oil vapours.

Organic surface contamination could be reduced to some extent by blowing clean air over the contact materials, although this treatment was only partially effective even at 100°C. An indication of the strength of the bonding processes involved is provided by the fact that adsorbed organic layers, as revealed by the ellipsometer, were completely removed only by vacuum annealing in the range 350 to 400°C.

Attempts were made to correlate the thickness, stability and refractive index of the adsorbed layers with the chemical characteristics of the lubricants from which the vapours emanated. The adsorbed layers examined had thicknesses which varied

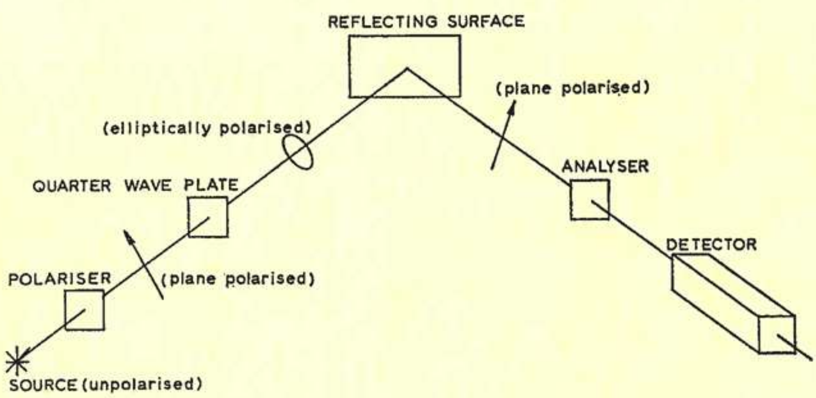

Fig. 2 The optical basis for the ellipsometer. Plane polarised light is transformed into elliptically polarised light, which is reflected from the specimen surface at an oblique angle. The initial polarisation characteristics are adjusted so that after reflection the light is plane polarised. The ellipsometer measures the ellipticity which has been extinguished by reflection, and from this the surface condition of the specimen can be determined. Both polariser and analyser are adjusted under servo-control to achieve the null (extinction) condition

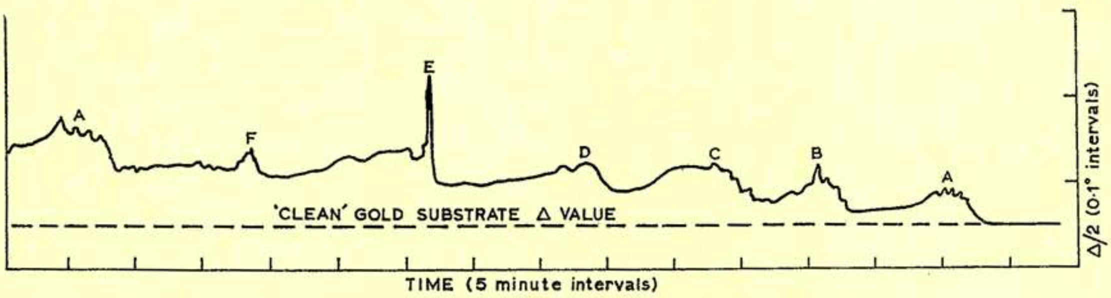

Fig. 3 Discontinuous development of contaminated layer on gold contact face caused by the adsorption of vapours from bottles of industrial lubricants A-F, the stoppers of which were removed at the time intervals indicated

- **A** **Neats-foot oil**
- **B** **Chlorinated paraffin wax**
- **C** **Mineral oil, chlorinated wax, petroleum sulphamate anti-oxidant and wetting agents**
- **D** **Naphthenic mineral oil with chemical additives**
- **E** **Solid wool fat in trichloroethylene with soap additive**
- **F** **Amine soap, sulphate of oil, mineral oil and aliphatic alcohol**

individually but which were all in the region of one monomolecular layer or less. Lubricants containing a substantial proportion of volatile compounds with highly polar groupings reacted strongly with the

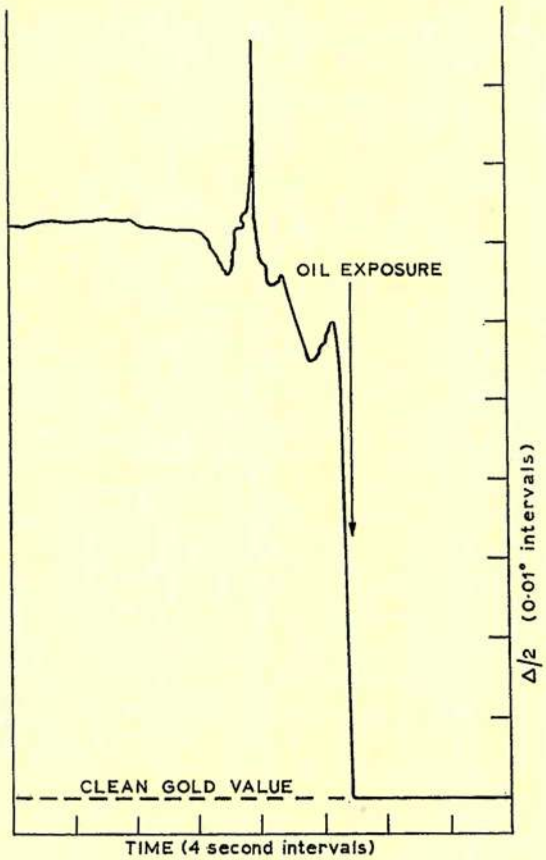

Fig. 4 Curve showing the very rapid adsorption of trichloroethylene from the vapour on to a clean gold surface

gold surfaces to provide very stable adsorbed layers. In particular, lubricant E gave every indication that it formed a layer on the gold surface that was more akin to a solid than to a liquid or to a gas. This conclusion was based on the high refractive indices which were measured. The infra-red spectrum of this lubricant corresponds closely to that of trichloroethylene with its characteristic chlorine bonds. The less polar groups produced adsorbed films which, although less stable, still had refractive indices higher than those associated with a gas.

The results of this work suggest that the cationic components of the lubricants interact strongly with gold surfaces, and that the adsorbed films thus formed are stable and have optical characteristics representative of solids rather than liquids. The less cationic components lend themselves to a surface state and structure more akin to vapours or to liquids. The films have a higher surface mobility and various degrees of persistence in their associations with the metal.

The best lubricant is likely to be that which reacts most strongly with the gold surface to produce a layer which effectively separates the metal from the forming tool. Formed contacts, therefore, are in danger of contamination at the surface and sometimes, one suspects, below it. A lubricant which does not provide a persistent film at the interface will, however, increase the surface friction level and reduce the efficiency of forming. The dual requirements of clean surfaces and of efficient metal deformation may therefore be in direct opposition, and conventional cleaning processes employing solvents such as trichloroethylene and other halogenated compounds can further complicate the problem. In many applications, therefore, cleaning by vacuum annealing may well offer a solution to users of contacts in highly sensitive circuits.

This work has demonstrated the usefulness of ellipsometry as a technique for studying the cleanliness of light duty noble metal contact surfaces.

However, as indicated earlier, ellipsometric techniques have much to offer in a wide variety of fields. Other studies are continuing on ion adsorption on gold in various environments with the object of throwing light on such important technological problems as environmental control and catalysis, and further studies on several aesthetic aspects of commercial gold surfaces have been initiated.

Ellipsometry does not provide all the answers to surface problems and it is usually best operated in conjunction with other techniques measuring important experimental parameters.

Acknowledgements are due to the Science Research Council under whose funding the ellipsometer was constructed and now operates.

Control of Particle Size in Gold Suspensions

Monodisperse suspensions of gold particles are often used in the study of particle size-dependent phenomena such as Brownian motion, light scattering, sedimentation and electrophoresis of small particles. A monodisperse system is a colloidal suspension in which all the particles are of effectively the same size. In many applications gold suspensions have the advantage of being relatively stable and chemically unreactive, but a knowledge of the particle size of gold suspensions is necessary before they can be used in further studies and it is an advantage to use a method of preparation that provides control of their size.

A method for the preparation of monodisperse suspensions of gold particles has now been developed by Dr. G. Frens of Philips Research Laboratories, Eindhoven (*Nature Phys. Sci.*, 1973, **241**, 20–23). The size of the gold particles can be controlled in the range 150 Å to 1500 Å. The method is based on the work of J. Turkevich et al. (*Disc. Farad. Soc.*, 1951, **11**, 55), who found that the reduction of chlorauric acid solution with sodium citrate gave a reproducible suspension of spherical gold particles within a narrow size range. The present work has shown that the number of gold nuclei formed at the start of the reduction depends upon the amount of sodium citrate used. Small amounts of citrate produce relatively few nuclei which then grow to form large particles as the residual gold in solution is reduced. Larger amounts of citrate produce more nuclei which grow to a less extent and produce small particles because the available gold is distributed over the greater number of nuclei.

Frens has shown that effect on particle size is dependent upon control over the relation between nucleation and growth and not on the amount of gold reduced from solution. He has done this by showing that the ratio of the number of gold particles per unit volume of suspensions of different particle size is in accordance with the same proportion of gold having been reduced in each case. The fact that no further change in the characteristics of the suspensions is caused by additions of more sodium citrate indicates that all the gold in solution is reduced. The technique of controlling the degree of nucleation is more convenient than methods that depend upon the use of a different nucleating agent before adding a reductant capable of causing growth only on existing nuclei.

Dr. Frens has used a series of suspensions of gold particles prepared by the new method to demonstrate the increased tendency of metal suspensions to coagulate in the presence of electrolytes as the radius of the particles increases. The uniformity of size and the regular spheroidal shape of the particles is shown in the electron micrographs of the smallest and largest particle size suspensions described. Similar regularity of particle characteristics is obtained when suspensions with intermediate particle sizes are produced.

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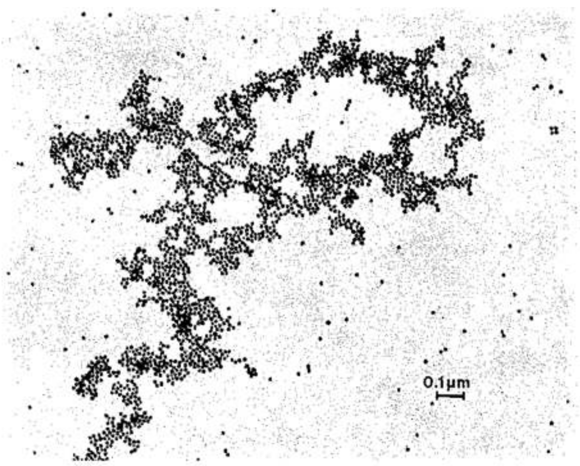
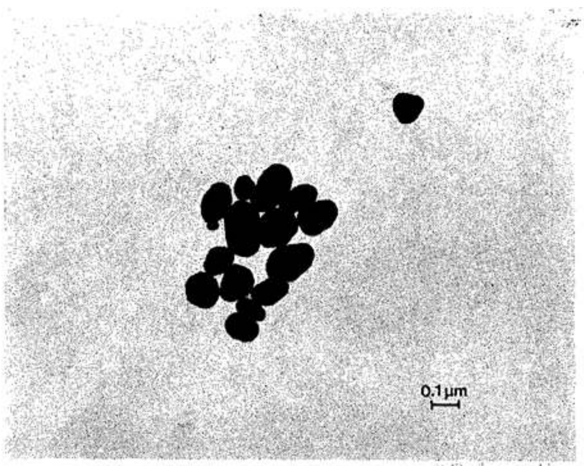


Electron micrograph of the finest gold suspension, with particle diameters of 160 Å



The largest of the range of six particle sizes, averaging 1500 Å in diameter