# Methods of Analysis of Structure of Electrodeposits

S. JOHN AND B. A. SHENOI
Central Electrochemical Research Institute, Karaikudi-623 006

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METALLIC coatings are often electrodeposited onto the surface of materials that include steels, zinc-base alloys, aluminium and plastics. The process is used when it is desired to obtain certain surface properties which the basis metal does not possess. Some of these properties are improved appearance, resistance to corrosion, resistance to wear, increased electrical conductivity and low contact resistance, improved frictional properties, specific metallic appearance and improved solderability. Many of these properties which determine their technological usefulness electrodeposits are structure dependent. For example, the surface structure is the principal factor which determines the brightness of electrodeposited metals. The corrosion resistance and mechanical properties are also greatly influenced by structure.

By structure is ment the arrangement of the atoms in the lattice, elastic displacement of the atoms, point defects, dislocations, stacking and twinning faults, grain boundaries and the surface morphology. In addition, structure includes the grain size, shape and orientation. The structure of electrodeposits is of fundamental significance because it is affected by such process variables as bath composition, current density, temperature, solution transport and the substrate and its preparation. Of primary importance is the role of foreign chemical substances in the plating solution, because these substances or their reaction products can be codeposited and thereby modify the structure of the plated metal. It is for this reason that addition agents are widely used in commercial plating applications where one wants to alter and control such engineering properties as brightness, internal stress, thickness uniformity or other mechanical and physical properties. Over the years a wide variety of experimental methods have been used to study the structure of electrodeposits relevant to such areas of application as decorative or protective coatings and electronic devices. The purpose of this paper is to summarise and critically review the methods used to obtain data on the structure of electrodeposits.

*Peculiar nature of electrodeposits from thermally prepared alloys :* Much of the earlier work on electroplating was confined to the morphological study of the electrodeposit and to the determination of the conditions required for the formation of deposits with some peculiar properties. Recent investigations have shown that the structure and physical properties of electrodeposited alloys are often different from thermally prepared alloys of similar composition. Moreover a change in electrodeposition condition may cause a substantial change of the phase structure of alloys even for those of the same chemical compsition.[1] There are several variables which have a significant effect on the phase structure of deposited alloys. These include the nature and concentration of the various ions in the solution, the electrolysis conditions such as over voltage and the overall process rate and the presence of surface active substances as well as thermodynamic properties of phases being formed. Hinton and coworkers[2] have shown that different types of defects such as twinning dislocations and packing defects are peculiar to crystals of electrodeposited metals. It is with such disorders that electric, magnetic and other properties are often associated. The formation of meta stable deposits through electrolysis enable one to produce alloys possessing special properties. Thus, for example, copper and bismuth as well their thermally prepared alloys are unable to pass into the superconducting state. However superconducting alloys may be prepared by electrolysis under suitable conditions.[3] Non-equiliburium phases are known to be obtainable by elecrochemical processes. It is reported that in electrodeposition of alloys, supersaturated solid solutions are often formed, the composition of which are beyond the solubility limits for equilibrium systems. Raub and Engel[4] have found this to be true of silver-lead alloys. In some cases, phases found in equilibrium diagrams at high temperatures only are formed by electrodeposition from solutions at room temperature. This process of formation of phases

corresponding to high temperature phases of thermal alloys can be explained from the fact that electrodiposited ions are always in a state of high energy due to over voltages associated with metal deposition.

*Microscopic methods :* The optical microscope hes been widely used to obtain information on the structure of electrodeposits. Metallographic cross sections are widely used today in industry to monitor the quality of plating processes by observing the grain structure and the thickness distribution in complicated geometries, as for example, plated through holes on printed circuit boards. When using this method it is virtually important to have samples which are properly polished and etched to reveal the microstructure. The optical microscope or metallograph is limited in its useful magnification to somewhere between 1500 X and 2500 X. The limit is determined principally by the optics and specimen. The maximum resolution is around 0.25$\mu$m but realistically should be considered to be closer to 1$\mu$m. Resolution depends strongly upon the numerical aperture, on the specimen preparation and contrast mode for observation. Metallographically prepared cross sections have been widely used in studies of electrodeposits leading to the development of a specialised vocabulary to classify the different types of observed grain structure. In this regard, the most important work is that of Fisher[3] who represented a classification scheme thirty years ago and that is still in use today and is responsible for such widely used descriptive terms as columnar, laminar, etc.

Most microscopic studies of metals are made using bright field illumination. In addition to this type of illumination, several special techniques like oblique illumination, dark field illumination, opaque stop microscopy, phase contrast microscopy and polarised light microscopy have particular applications for metallographic studies. Figures 1 and 2 illustrate the columnar and laminar types of micro structure as seen in cross sections of plated copper with the optical microscope. The structure of Fig. 1 was produced in an additive free plating system used for the manufacture of printed circuits. The use of Normarski interference contrast is responsible for the fine detail observed. This method is particularly well suited ror the characterisation of very smooth electrodeposits with features such as growth steps in the range 5-20 nm in height and has therefore been used in electrocrystallisation studies[5]. The laminar or banded structure in Fig 2 resulted from the addition of benzotriazole to the plating bath.[7] The multiple beam interference



Fig. 1. Optical micrograph of Columnar structure in cross section of copper plated on printed circuit

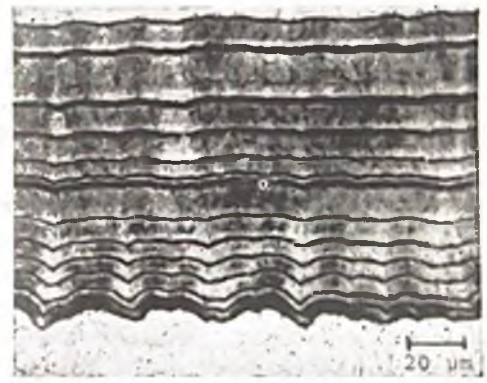



Fig. 2. Optical micrograph of laminar structure in cross section of copper deposit from sulphate bath with benzotrizole[7]

microscope developed by Tolansky[6] has achieved great popularity in the last ten years because ef its extreme sensitity and elegance. The power of the Tolansky technique has been recognised and exploited by those who study crystal growth and imperfections but has been much neglected by those who work in electrodeposition.

*Electron microscopy :* The essential difference between the light and electron microscopy arises from the wave lengths used. The wave lengths that are commonly used are as follows :

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|---|---|
| Light microscopy | 3500 7000 A° |
| X-ray diffraction | 1-2 A° |
| Electron microscopy | 0.5-0.07 A° |

The extremely short wave lengths of the electron beam is responsible for the high resolution

obtained in the electron microscope. The resolution of current transmission microscopes (TEM) is 0.2 nm while that of the scanning electron microscopes (SM) is approaching 10nm. Each of these powerful instruments provides information about the structure of electrodeposit and both are widely used today.

*Transmission electron microscopy :* The techniques of electron microscopy are also well known and have been summarised and referenced[11]. The TEM is the principal method of elucidating the defects in electrodeposits Features such as dislocations, twinning and grain boundaries produce diffraction contrast and are therefore clearly evident in TEM images. Direct observation of organic molecules incorporated in electrodeposits by transmission electron microscopy was first reported by Albert, Schneider and Fischer[11]. They employed the so-called through focus imaging technique in which the image of organic molecules in metal matrices is observed under defocussed conditions. Nakahara and Okinaka[12] review the theory of defocusing contrast and describe experimental results obtained with electroless copper, electrolytic copper and electrolytic hard gold deposits. Gas bubbles were observed in electroless copper diposits, whereas electrolytic copper and hard gold deposits contained numerous organic molecules that were uniformly distributed. The through focus imaging technique was also coupled with stereomicroscopy in order to obtain information on the spatial distribution of the phase objects. The dark field technique offers several advantages in the characterisation of electrodeposits. For example, high resolution dark field images provide the most unambiguous method of determining grain size in the range of 1-20 nm. The continuing research concerning the nucleation and growth of electrodeposits has been closely coupled with the experimental capability of modern TEM. The studies of Nakahara and Weil[13] has shown that the initial structural features which form when Ni is plated on copper consists of three dimensional epitaxial crystallites (TEC). These features are considered to be important because their growth and subsequent coalescence provides a mechanism for the generation of dislocations. Experiments of this type are facilitated by the use of thin foil substrates which can remain intact so that the earliest stages of deposition prior to the formation of a continuous film may be investigated.

Sard[14] observed the initial stage in the formation of an electroless copper deposit on a thin amorphous carbon substrate which was catalysed by the adsorption of tin and palladium. The structure at this stage consists of clusters ($\sim$ 30 nm across) comprised of small crystallites ($\sim$ 3nm dia) which were deposited on the heterogeneous catalyst particles. Continued metal deposits formed by this process exhibit an extremely heterogeneous structure with grains too small to be resolved by optical microscopy; yet they are certainly not amorphous, despite statements in the literature to be contrary. Certain commercial electrodeposits of hard gold, which also have an exceedingly fine grain size have been erroneously called amorphous. To elucidate such fundamental aspects of defect structure as the dislocations, Burgers vector, point defect clusters, twin faults, structure of grain boundaries and the detailed features of planar faults in electrodeposits. one must utilise the three complimentary imaging modes of bright field, dark field and selected area diffraction in conjunction with tilting experiments to determine precisely the diffracting conditions responsible for the observed changes in contrast. The details of this aspect of the subject can be found in standard references[10].

The development of high voltage TEM (e g. 1 MV) has led to a growing interest in quantitative metallographic techniques. Combined with stereo imaging techniques this instrument can provide more information about the three dimensional arrangement of structural features than is possible with conventional 100 KV instruments. A recent publication gives some examples of studies of electrodeposits with the MV TEM[15].

The surface morphology of electrodeposits has been studied extensively by several electron microscopic methods. In the 1960's, replica methods were used in conjunction with the TEM, to characterise surfaces in relation to such properties as brightness[16] and corrosion resistance[17] and to the plating variables[18-20]. The replica technique offers the advantage of relatively high resolution ($\gtrsim$ 3 nm under optimal conditions) and the disadvantages of a complicated preparation procedure.[21] A technique using transmitted electrons for imaging surface features on the molecular scale has recently been disclosed. This method will undoubtedly find application in fundamental

studies of the growth steps on the surface of electrodeposits[22].

*Scanning Electron Microscopy (SEM) :* In our rapidly expanding technology, scientists and engineers are often required to observe and correctly explain phenomena occuring on a micrometer ($\mu$m) and submicrometer scale. The scanning electron microscope (SEM) and electron probe-micro analyses (EPMA) are two relatively new and powerful instruments which permit the characterisation of heterogeneous materials and surfaces on such a fine scale. Among the major types of information obtained are compositional information of both a qualitative and quantitative nature and topographic information contained in images obtained at relatively higher resolution. The SEM and EPMA are in reality, one and the same instrument and can be treated as such. The use of SEM and EPMA has increased markedly over the last few years and the number of scientific papers dealing with the theory and practical application of the two instruments has also increased.[23-25]

The conventional scanning electron microscope is designed to operate in the back scatter mode. The primary beam of electrons is made to scan the specimen surface and either the back scattered electrons or the low voltage secondary electrons are collected and used for image forming. In the latter mode of operation, instruments with a guaranteed resolving power of 150 Å can be purchased. Interest is now developing in the use of back scattered electrons for image formation, particularly for non-conducting specimens.

The magnification achieved with SEM ranges from that of the optical microscope (20×) to that of the electron microscope ($10^5$×) and its depth of focus is at least twenty times greater than that of the optical microscope. Thus it is possible to look at odd shaped objects at high magnifications while keeping the entire object in focus. For good electrical conductors, no specimen preparation is needed ; for insulators or poor conductors a thin metal film evaporated onto the surface will prevent charging.

In printed circuit industries the bond strength between the copper foil and the base material is one of the most important factor for copper clad laminates. Several post treatment methods have been proposed for modifying the surface crystallinity for improved bone strength[7]. It is well known that the more uniform the distribution of particles over the surface and the higher the peak to valley depth, the greater is the bond strength between the laminate and copper foil. The present authors[26] studied the surface morphology by scanning electron microscopy in order to ascertain which treatment gives uniform distribution of grains, with appreciable peak-to-valley height over the surface. SEM studies has shown that anodic treatment in hot alkaline solution gives a surface wherein the particles are protruding upto a greater height and indicate a hill and valley structure of the surface. Fig. 3 shows the nearly three dimensional image of copper foil treated with sodium hydroxide solution.



Fig. 3. Secondry electron image of copper foil treated with sodium hydroxide solution

An energy dispersive X-ray unit can be added to an SEM, so that the specimen surface can be chemically analysed as well as viewed. The X-ray energy spectrum may be used for quantitative analysis with suitable standards. When it is difficult to ascertain whether a detail under examination is a protrusion from the surface or a pit or crevice, stereo microscopy with the SEM is most useful[23]. This technique is simple and has been used to study pitting and crevice corrosion and intergranular corrosion.[8] SEM images have also been used to elucidate the mechanism of bonding between the electrodeposit and non conductors in the field of plating on plastics.[9]

*Electron Proble Micro Analyser (EPMA) :* This instrument is a tool[9,30-31] for the elemental analysis of small particles or for measuring changes in composition along the specimen surface. Its resolution is of the order of 1-2$\mu$m, making it suitable for analysing foreign impurity contaminants, corrosion products etc on electrodeposits and micro electronic devices[3,4,5]. The energy dispersive X-ray analyser, discussed above is one type of electron microprobe. Most microprobes

unlike SEMs have an optical microscope with a calibrated stage so that the specimen may by viewed, any area may be accurately located and distances between areas may be accurately measured.

The microprobe uses a focussed electron beam to excite x-rays in a limited volume of the specimen. The elements present in this volume interest with the electron beam which results in part, in the emission of energy in the form of X-rays. Since each element emits X-rays with energies which are fixed by the energy levels of the electrons of the element itself, the wave lengths of these x rays are fixed and unique for each element. The intensity of these emitted x-rays is a function of the atomic per cent of the element in the particular volume being excited by the electron beam. The resolution of the microprobe is limited principally by the finite diameter of the electron beam, the accelerating voltage for the electron beam and the elements in the sample itself. Since electrons striking the specimen may penetrate to a depth of the order of microns, depending upon their accelerating voltage X-rays will be generated in a volume of materail. The beam diameter is an important factor that determines the volume of material from which x-rays are generated and hence the resolution. Of equal importance to a microprobe analysis is the sensitivity. Again it is said that the microprobe can detect some elements at concentrations as low as 50 ppm but this is achievable only in a finely tuned instrument for high atomic number elements Elements with atomic numbers lessthan magnesium for examples are detectable only at levels above 0.1%. A quantitative analysis of the intensity data is a time consuming process. The measured or recorded X-ray intensities must be corrected for background detector non linearity, absorption, atomic number effect and flourescence. These corrections are expressed as multiplying factors which are applied to the uncorrected intensities to determine the weight concentration of a particular element[36,37].

Figure 4 shows the cross section of a thin electrodeposit ($\sim 0.6\mu m$) on a piece of commercial silverware. The X-ray spectrum indicates the presence of Au and Ni in addition to Ag. Two additional methods of displaying the X-ray information namely elemental maps and line scans are often helpful when the species is segregated[19]. The extension of this type of instrumentation to studies of diffusion is discussed by Owen[39]. This technique has been used to detect contamination on electrical contacts in micro electronics[40].



Fig. 4. X ray line scans for gold, silver and nickel

Surface contamination of electrodeposited gold can arise by diffusion of the basis metal and the consequent formation of insulating oxide films. This form of dagradation of a contact surface has been recognised for a long time, its severity depending upon both time and temperature, and a barrier layer or underplate of nickel is often used as a reasonably effective means of retarding diffusion and the eventual failure of the contact. Pinnel and Bennett[38] investigated the diffusion behaviour of nickel under coats over a wide range of temperatures by the microprobe analyser using X-ray wave length dispersive analysis on polished cross sections and scanning the electron beam along a path at right angles to the Cu-Ni and Ni-Au interfaces. Their work confirms the effectiveness of nickel as a diffusion barrier, but only to the extent that it retards but does not wholly prevent the diffusion process ; the time necessary for copper to diffuse to the gold surface at a given temperature is longer with the nickel layer than without it. Thus work clearly brings out the fact that increasing nickel thickness increases the time necessary for the diffusion of copper to the surface.

*Other electron and ion beam techniques :* Many recently developed methods are likely to pay important roles in future for quantitative surface analysis. Among these are electron spectometry, ion scattering spectometry, and secondary ion mass spectrometry for the analyses of films in the submono layer thickness range and in the multilayer range, Rutherford back scattering is useful for the analysis of films with thicknesses from 500 to 5000 A°.

The technique of Auger Electron Spectroscopy (AES) has developed rapidly during the past few years into routine analytical technique for determining the elemental composition of solid surfaces and the indepth elemental composition of thin films. The application of AES to practical problems began expanding mainly through developments in instrumentation. The introduction of cylindrical Mirror Analyser (CMA) significantly reduced the time required for analysis, Simultaneous AES and ion sputter etching for indepth compositional analysis or thin film analysis has been introduced by including a sputter ion gun directed at the analysis point on the sample. The time required to perform thin film analysis has been further reduced by the addition of an Auger peak multiplier and point plotting system which automatically plots the peak to peak amplitude of preselected Auger peaks during ion etching. Scanning Auger (Microprobe (SAM) technique has been developed. This technique increases the lateral spatial resolution of AES while maintaining the ultra high vacuum environment and the thin film analysis capability of previous AES thin film analysis systems[41].

Electron spectrometry or Electron Spectrometry for chemical Analysis (ECSA)[44] involves the high resolution measurement of the energy spectrum of electrons ejected from the surface and near surface region when a specimen is bombarded with a monoenergetic beam of X-rays or electrons. The analysis of the X-ray induced photo electron spectrum has been given the acronym XPS while the measurement of the secondary electron spectrum is called Auger Electron spectrometry as discussed above. Several applications of electron spectrometry to corrosion studies have been reported recently[42-43].

Other new techniques include[25,45-48,55] ISS (Ion Scattering Spectrometry) SCANIIR (Surface Composition by Analysis of Neutral and Ion Impact Radiation), Ion Beam Mass Spectrometry, Low Energy Electron Diffraction, Reflectance Higher Energy Electron Diffraction have been used to characterise some of the more fundamental aspects of the structure of electrodeposits[49]. For example, differential reflectance spectroscopy provides information about the electronic structure[50]. A related optical measurement which is much more straightforward is that of reflectance using a conventional spectrophotometer. This method has been used to characterise the roughness of bright nickel deposits[51] and was shown to agree with results of surface replica studies by TEM. A similar correlation has also been demonstrated for electroless gold deposits[52]. A more detailed discussion of this topic is given by Young Teaque[53]. Finall Mossbauyer Spectroscopy has been used to identify compound formation valence and nuclear effects in several of the systems which lend themselves to this method[54] has been used to good advantage recently[55] in studies of tin-palladium colloid species which are used routinely in electroless plating.

*X-ray diffraction methods* : X-ray diffraction is the scattering of X-rays by matter with accompanying variation in intensity in different directions due to interference effects. X-ray diffraction is one of the most important tools of solid state physics since it constitutes a powerful and readily available method for determining atomic arrangements in matter. X-ray diffraction methods depend upon the fact that X ray wave lengths of the order of 1Å are rapidly available and that this is the order of magnitude of atomic dimensions when an X-ray beam falls on matter, scattered X-radiation is produced by all the atoms. These scattered waves spread out spherically from all the atoms in the sample and the interference effects between the scattered radiation from different atoms cause the intensity of the scattered radiation to exhibit maxima and minima in various directions. Some of the uses of X-ray diffraction are :

a) differentiation between crystalline and amorphous electrodeposits, b) determination of structure of electrodeposits (crystal axes, size and shape of the unit cell, position of the atoms in the unit cell), c) determination of electron distribution within the atoms and throughout the unit cell ; d) determination of orientation of single crystals, e) determination of the texture of the polygrained electrodeposits f) identification of crystalline phases and measurement of the relative proportions g) measurement of limits of solid solubility and determination of phase diagrams h) measurements of various kinds of randomness disorder and imperfection in crystals i) determination of radial distribution functions for amorphous solids and j) measurement of elastic strain effects and small grain size.

*Crystal structure*: The arrangement of atoms in the lattice is determined from Bragg's law $\lambda = 2d \sin\theta$, which yields the spacing of crystal planes (d) from the measured scattering angle($2\theta$) for a coherent beam with known wave length ($\lambda$). Many standard text treat the subject of crystal structure analysis by X rays[56,57] and by high energy electrons[58]. The arrangement of atoms in the surface region can be determined with high energy electrons ($\geq$50 Kev) at glancing angles of incidence (RHEED) or with low energy electrons ($\geq$500 ev) at normal incidence (LEED). The latter method has been used in studies of the structure and epitaxial growth of evaporated films on single crystal substrates[59,60]. Both the science and technology of crystal structure determination are well developed for single crystals and randomly oriented polycrystalline aggregates. However, there are two complicating factors which are characteristic of the structure of electrodeposits, namely a) elastic strains which displace the atoms from their equilibrium positions and b) preferred orientations or textures, which means that the different crystallites or grains comprising the polycrystalline aggregate are not randomly oriented as they are in a powder. much has been learnt about these two factors from careful measurements of diffraction line positions and intensities. The experimental details of making these measurements and the interpretation of the results for thick films and bulk meterials are well reviewed in the literature[56-58]. The experimental considerations relevant to the analysis of thin films by X-rays have been reviewed by Bertin[61] and the latest advances in the application of X-ray methods of studies of crystal perfection in films 15 nm to 1 $\mu$m thick have recently been reviewed by Dobrott[62]. The thickness range from about 10 to 50 nm is suitable for the transmission of 100 KV electrons and films upto $\sim$1$\mu$m can be studies by MV electrons. The experimental details and procedures for the analysis of the crystal structure by electron diffraction are also covered in the literature[58,63].

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