CHAPTER I

INTRODUCTION

1.1. HISTORICAL

Oriented overgrowth of one crystalline specy over another was first discovered by minerologists in 1817. Any two crystals of different species were found to grow with some definite and unique orientation relationship between the two crystal axes. In the early days, the investigations of this phenomenon were characterised by macroscopic studies. Generally, a rational plane was found along which the two crystals were intergrown. Comprehensive lists of examples of oriented overgrowth have been reported by Wallerant (1902) and Mügge (1903).

Such observations obviously led to attempts to observe the oriented growth in the laboratory. Frankenheim (1836) was the first to succeed and found that sodium nitrate grew from solution in parallel orientation on calcite. Barker (1906, 1907) systematically studied the growth of alkali halides upon each other. Royer (1928) repeated much of the work of Barker and extended it to cover many other examples of growth from solution. He introduced the term epitaxy (arrangement on) to denote the phenomenon of oriented growth from solution or vapour phase. The discovery of X-rays at about the same time greatly advanced the knowledge of
crystal structure. As a result, an important foundation for structural proof of the observed phenomena was laid by Royer who introduced the idea of percentage misfit defined as \(100(b-a)/a\) where \(a\) and \(b\) are the corresponding network spacings in the substrate and the overgrowth respectively. On the basis of his observations, Royer advanced three rules of epitaxy, the most important of which is that oriented growth may occur provided the parallel lattice planes of the two crystals have networks of identical or quasi-identical form and the misfit is small.

The advent of electron diffraction vastly improved the scope of epitaxial studies. Electron diffraction technique is particularly suited for the study of surfaces. In addition to growth from solution, many other methods were adapted for growth such as, electro-deposition, vacuum evaporation, chemical attack.

Comprehensive reviews of the epitaxial growth studied by optical microscopy with a few by X-rays have been published by Van der Merwe (1949) and Seifert (1953). A comprehensive and critical account with extensive lists of examples of oriented growth studied exclusively by electron diffraction is given by Pashley (1956).

1.2. THEORIES OF EPITAXY

Finch and Quarrel (1933-1934) introduced a new concept of basal plane pseudomorphism as a result of their studies on the growth of zinc oxide on zinc. This involves the formation of an initial oriented film which has an abnormal crystal
structure. The first lattice planes of the growth parallel to the substrate are assumed to be identical in size to that of the substrate so that an appreciable number of layers of the deposit are deformed under the strain.

Following this concept, Frank and Van der Merwe (1949) developed a general theory of epitaxy. However, the validity of the concept of pseudomorphism has been questioned by Thomson (1939) on the grounds of insufficient evidence and by Pashley (1956) on the basis of experimental evidence obtained from the study of electron diffraction patterns of extremely thin films of the order of 0.1 to 10 Å on average.

Engel (1952, 1953) put forward a theory in a restricted form for the epitaxy of metals upon ionic substrates, in which an attempt is made to explain the observed misfits and the dependence of orientation on temperature.

Dixit (1958) has put forward a theory of epitaxy of metals which is essentially an extension of the theory put forward by him for the oriented growth on amorphous substrates (Dixit 1933). It is assumed that metal atoms during deposition behave like a two dimensional gas and obey an equation similar to the Van der Waal's equation. For crystalline substrates, an additional term for the force of attraction between the atoms of the deposit and the substrate is taken into account. Without making any arbitrary assumptions about the misfit, an expression for the misfit is obtained. In the present state, the theory is limited in its applications to the deposits of only metal atoms on crystalline substrates.
1.3. METHODS OF STUDYING EPITAXY

1) Optical microscope: - In the early days, the optical microscope was invariably used for the study of growth from solution. Because of the limitations of the resolving power of the optical microscope, the size of the crystallites of a deposit must be of the order of a few microns. The orientation of each crystallite, if it possesses a well defined external form, can be determined with respect to the substrate.

2) X-rays: - This method leads to the direct determination of the orientation of the crystallites of the growth, in which any knowledge of their external form is not necessary. Sufficiently thick growth is, however, essential to get a photograph in a reasonably short time.

3) Electron diffraction: - Most of the work on epitaxy is carried with fast electrons (30 to 60 K.V.). The reflection technique is most suitable and is commonly employed. The transmission technique may also be used. The electron diffraction method has distinct advantages over other methods employed for the study of epitaxy. Very thin films of the order of 5-10 Å on a suitable substrate can give intense reflections which are clearly visible on the fluorescent screen. The patterns due to the growth can be examined in various azimuths.

1.4. INVESTIGATIONS OF OTHER WORKERS ON OXIDE GROWTH ON COPPER

Because of its technical importance, oxidation of copper has been extensively investigated by various workers.
In his report, Mügge (1903) describes layer deposits of oxide on natural copper. He found that oxide grows in parallel orientation on copper. Thomson (1931) found the oxide growth in parallel orientation on copper faces oxidised by anodic treatment and examined by electron diffraction. By X-ray examination of single crystals of copper oxidised in air at high temperature, Mehl and his coworkers (1934) reported that the oxide film is formed merely by an expansion of the copper lattice without any change in the orientation. These early investigations were characterised by the oxide growth produced on rough copper faces which were obtained by employing routine chemical echants.

With the advent of electrolytic polishing of copper, surprisingly new orientations of oxide were found. The investigations of the oxide growth on the spheres of single crystals of copper by the school of Kossel (1952), revealed some interesting orientations of oxide. A parallel orientation of oxide was observed on (110) copper face pole and anti-parallel orientations on other face poles (001), (111) and (113). Kossel seems to be the first to have recognised the anti-parallel nature in the oxide orientations.

Frisby (1947, 1948) studied the oxide growth on electrolytically polished copper faces which were oxidised in boiling water. The results of his investigation are similar to those of Kossel.

Pinsker (1953) in his experiments on formation of oxide on single crystal films of copper examined by transmission of electrons observed that oxide accurately orients...
in parallel orientation on copper films.

Gornyi (1956), Goswami and Trehan (1956), and Trehan and Goswami (1958) studied the oxide growth on electrolytically polished copper faces (110), (001) and (111) by electron diffraction and found the oxide orientations similar to those observed by Kossel. Goswami and Trehan studied the orientations of oxide formed at various temperatures in air in the range 100° to 280°C and found that the orientations remain unaffected.

1.4A. Methods of oxidising copper:

The most commonly employed method of oxidising copper is the application of high temperature from 100° to 1000°C at various pressures of air. Frisby oxidised copper crystals in boiling water. Thomson employed the anodic treatment for oxidation of copper faces. Immersion in solutions of ionic salts produces quite thick oxide films on copper. Exposure of copper to sunlight immersed in a dilute solution of copper salt produces thick oxide films exhibiting beautiful interference colours.

1.5. Scope of the present work

In this study of oxidation of copper faces, two methods are adapted for the preparation of the copper faces.

1) Chemical etching by a suitable etchant after mechanical polishing. This method, however, produces a surface with a high degree of roughness.

2) Electrolytic polishing in suitable electrolytic baths. This method imparts a high degree of polish to the surface on
The intermediate stages of the nature of the copper faces from a high degree of polish to a high degree of roughness have not received much attention in the study of oxidation. In fact, the studies of the oxide growth on such surfaces by electron diffraction are likely to yield detailed information about the oxide orientations both by primary and secondary diffractions from the various facets developed by etching. On some of the copper faces, the oxide growth is observed to be in parallel orientation when roughly etched, but in antiparallel orientation when electrolytically polished. The present investigation was undertaken with the expectation that the study of oxide growth on copper faces with various degrees of roughness may throw more light on the surprising behaviour of oxide orientations mentioned above. The oriented growth of oxide on electrolytically polished copper faces etched to various degrees of roughness is investigated by electron diffraction reflection technique. In all nine copper faces from \([\{110\}]\) zone are employed in this study.

To carry out this work, the following experimental set up is essential and was accordingly built up:

1) A tubular furnace, workable up to 1150°C, was constructed in which single crystals of copper were grown in a vacuum of \(10^{-2}\) mm. of Hg., following the slow cooling method of Thomson (1931).

2) An electron diffraction camera of Thomson-Fraser design with a hot cathode was designed and built.
3) An optical goniometer suitable for cutting a crystal parallel to any crystallographic plane, in addition to being suitable for measurement of interfacial angles was designed and constructed.

4) A jig was constructed to grind the crystal face accurately after determining the inaccuracy by electron diffraction.

5) A small electrolytic cell was fabricated from polythelene tubing and sheet for polishing of copper faces.