SOME APPLICATION IN ELECTRON MICROSCOPY

"Nucleation and Growth of Copper Thin Films
Deposited on Cold Substrates"

THESIS

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بسم الله الرحمن الرحيم

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SUMMARY

In the present work transmission electron microscopic observations of copper thin films formed by vacuum deposition on carbon, mica, and rock salt substrates, were investigated. The growth mechanism of such thin films concerning the various stages of nucleation, coalescence, channel and hole formation was discussed. Statistical analysis of particale population and particle size distribution has helped to give a clear picture of such mechanisms in case of films having thicknesses varying between 20 - 150 Å.

The main results of this investigation were:

1- Various stages of growth of copper thin film condensed on various substrates were found to consist of nucleation, coalescence, channel formation, and hole formation before continuous film is formed.

2- Clustering and coalence of nuclei were found to lead to particles, combination of particles and nuclei were found to lead to large particles, and clustering of large particles were found to lead to islands, and coalesence of islands and combination of islands and nuclei were found to lead to channel formation.

3- The islands and particles were found to have denuded regions arounds them indicating that the coalecence process is associated with a decrease in surface coverage.

4- As the film thickness was increased, the average particle size was found to increase, the average particle population was found to decrease and the surface coverage was found to increase.

5- Electron diffraction analysis of copper thin films deposit-ed on carbon substrate showed polycrystalline structre.

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I N T R O D U C T I O N

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[illegible] electron microscopy provides a [illegible] tool for studying the microstructure of thin metalic films at various stages of their growth, so that their mode of growth can be examined in some details.

The preparation of thin metalic metal films by deposition is an important subject, since the optical, electrical, and magnetic properties of these films make them of considerable theoretical and technical interest. They are used in manufacturing transistors, capacitors, and interconnections. They are also applied in the microcircuits of reporting, amplifying, switching, and memory recording.

There are four general ways of carrying out the deposition, 1) vacuum evaporation; 2) electrodeposition; 3) sputtering; and 4) chemical attacks. The vacuum evaporation technique is the most widely used method.

The standard work on vacuum deposition given by Holland[1] (1956), Bassett[2] (1961), and Pashley[5] (1964) has the advantage of that large uniform area of films of controlled thickness can be prepared, besides the dependence of the film crystal orientation to some extent on that of the substrate. A single crystal substrate can then lead to a single crystal deposit. This phenomenon is known as epitaxy (Pashley[4], 1956).

[illegible] the growth [illegible] films by [illegible] the choice of a suitable substrate is much more limited, and is governed by the following conditions :
1) The surface must be smooth and clean; 2) the deposited metal must grow on it epitaxially in a convenient orientation; 3) the possibility of dissolving the substrate without appreciable dissolution of the deposited film; and 4) the deposited film should be continuous at the required thickness

A suitable clean smooth surface can often be obtained by using a freshly cleaved crystal[5]. Alternatively, polished surfaces can be prepared mechanically, and the worked layer suitably removed[6]. Optically smooth (100), (110), and (111) faces of rock salt were obtained by a suitable polishing technique, and the produced surface layer was removed by thermal etching of the surface at 350°C in vacuo. Excellently oriented films of copper were formed by deposition onto these surfaces.

Deposition is commonly carried out in demountable vacuum system[6,7,8] with an ultimate vacuum of about 10^{-5} mm Hg. At this pressure the rate of bombardment of a substrate surface by the residual gas molecules is comparable with the rate of arrival of the deposited vapour molecules, so that [illegible] deposit [illegible]. Also, it is possible that the presence of [illegible] gas has some effect on the mode of the growth[10], and hence the microstructure of the deposit. So it is much better to prepare such films in much cleaner vacuum systems with ultimate pressure as low as 10^{-10} mm Hg[11]. This involves much more careful and prolonged experiments, and it is too early to judge the advantages of these cleaner systems. Anyhow deposition in a vacuum system of 10^{-5} mm Hg is relatively straight forward and quick to carry out, and leads to good quality films in many cases.

The structure of the deposited film is considerably influenced by the temperature at which the substrate is maintained during the deposition. Elevated substrate temperature produce films with large grain size and when single crystal substrates are used, oriented growth is more likely to occur at the higher temperatures[12].

Particulary for the growth of single crystal films, it is necessary to ensure that no contamination can be readily deposited if, for example, low melting point metals exist as an impurity as a component of the heating device[13]. The control of the thickness demands careful attention. There are two basic methods of control, either by loading the source with a known amount of material to be totally evaporated, or the source contains more than required, and the amount deposited is determined by some independent calibration. The difficulty with the former method is that the efficiency of most sources varies considerably as a function of direction as was shown by Preuss[14] (1953). A given source can be calibrated by a subsidary experiment, thus it becomes easy to calculate the thickness on a given specimen from the amount of the evaporated material.

Double evaporation techniques are sometimes useful. Good single crystal films of gold have been prepared by first depositing about 1500 Å of silver onto mica or rock salt, and then depositing the required amount of gold onto the silver[12]. The gold films are readily detached by dissolving the silver in nitric acid. Uniform coherent films of any thickness from about 100 Å upwards, can be obtained in this way in (111) or (110) orientation. Similarly, good thin crystal films of nickel have been grown by first depositing copper on rock salt, and then nickel onto copper[15].

When a surface film is grown by the evaporation method, the molecules arriving at the substrate surface have enough thermal energy, and a high surface mobility. This causes the molecules to migrate over the surface and aggregate into small stable groups of nuclei, as discussed by Franklin[16] (19[illegible]). The initial nuclei are frequently observed to be three-dimensional, so that growth does not proceed atomic layer by atomic layer.

Because the saturation of the vapour in the vicinity of the substrate is high, there is no necessity for the substrate surface to have imperfections to allow condensation and growth to occur. Homogeneous nucleation will occur readily on an ideal smooth substrate. However, when surface imperfections exist on the substrate surface, they are sometimes found to act as sites for preferential nucleation of the deposit.

It was found by Bassett[17] (1958), and consequently confirmed by Sella and Conjeand[18] (1959), and others, that gold nuclei form preferentially at steps on a rock salt cleavege surface.

The various stages of copper thin film formation were found to be similar to those reported recently about gold and silver thin films on various substrates. Pashely[19] (1959), Bassett and Pashely[20] (1959), Bettows[21] (196[illegible]),

[illegible] (1965), [illegible] and Grünbaum[illegible] (1965), Summer[12] (1965), and Kazwhio and Yukio[24] (1966) .

The formation of three-dimensional stable nuclei has been discussed by Poshely et. al[25] (1964). The atoms or molecules incident from the vapour source will be adsorbed on the substrate and readily reach thermal equilibrium. The adatoms diffuse in the substrate and interact to form a polyatomic cluster. Some clusters or embryos will grow and form clusters of a critical size which condense out as stable nuclei. The rate of nucleation is extremely dependent on the adatom population. A critical supersaturation is required for large rates of nucleation to occur. The nuclei are formed at preferred sites such as the end of dislocations or at surface defects in the substrate as has been observed in the growth of copper on hot silver (Kohoe et. al[26] ,1956).

Although it was deduced that in the majority of these cases, isolated nuclei are formed during the initial stages of growth of an evaporated film, no systematic evidence could be obtained to show how the size, shape, and distributions of the nuclei varies according to the substrate upon which the film is formed. Also it was observed that after the initial formation of discrete crystallites on a substrate surface, subsequent deposition leads to an increase in size, and growth of these crystallites, until a continuous film is eventually formed, but the detailed manner in which this occurred was not studied or explained before[12,23,24].

The aim of the present work is to study the sequence of nucleation and the growth of copper thin films formed by evaporation inside a normal coating unit on different substrates. Also to study the effect of these substrates on particle size, particle population, and the percentage of surface coverage.

C H A P T E R I

E X P E R I M E N T A L T E C H N I Q U E S