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THE NUCLEATION AND GROWTH OF TUNGSTEN THIN FILMS VAPOR
DEPOSITED ON VACUUM-CLEAVED ROCK SALT SUBSTRATES

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MASTER

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94

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
A. Recent Advances in Thin Films	1
B. Purpose of the Investigation	10
II. EXPERIMENTAL	12
A. Apparatus	12
B. Evaporation Rate	16
C. Type of Experiment	18
D. Typical Runs	18
III. RESULTS	21
A. Vacuum-Cleaved NaCl	21
1. Substrate at 350°C	21
2. Substrate at 250 and 150°C	30
3. Substrate at 25°C	31
4. Substrate at 450°C	32
5. KCl Substrates at 350°C	33
B. Air-Cleaved Substrates	35
1. Substrate at 350°C	37
2. Substrate at 25°C	38
IV. DISCUSSION	40
A. Growth Modes	40
B. Polymorphic Variants	42
C. Orientations and Morphologies of Tungsten Thin Films ..	46
V. CONCLUSIONS	49

LIST OF TABLES

Table		Page
I	Comparison of Growth Characteristics and Polymorphic Forms by BCC Metals.	55
II	The s-Values of Maxima of the Evaporated Carbon Films and Some (hkl) Reflections of Tungsten.	56
III	Sublimation Rates of Cleaved Sodium Chloride.	57
IV	Calculated Spacing of the hkl Rings of Both α - and β -W Structures.	58

I. INTRODUCTION

A. Recent Advances in Thin Films

In 1958, Bauer⁽¹⁾ developed a classification scheme for the growth of thin films. This scheme distinguishes among three basic growth modes: the Volmer-Weber mode, the Frank-van der Merwe mode, and the Stranski-Krastanov mode, as illustrated in Figures 1a, 1b, and 1c. This classification is based on the strength of the interfacial interaction between the deposit and substrate. The first mode should occur whenever the interfacial interaction between deposited atoms and substrate is weak, compared to the cohesive interaction among deposited atoms; this mode is often referred to as the "weak interfacial interaction" growth mode. Some good examples of such a growth mode are Ag and Au on NaCl and LiF. The second mode is the reverse of the first one; it should occur whenever the interfacial interaction is strong, compared to the cohesive interaction among deposits; this mode is also often referred to as the "strong interfacial interaction" mode. Ag on W⁽²⁾ and fcc metal deposits on fcc metal single-crystal substrates^(3,4) are good examples of the Frank-van der Merwe mode. Finally, the last mode corresponds to the borderline case between the first and the second mode, that is, between "strong" and "weak" interfacial interaction. The case of homoepitaxy,⁽⁵⁾ Ag on Si and Ag and Au on Cu⁽³⁾ correspond to this mode.

Since thin epitaxial films frequently present some interesting properties (magnetic, electrical, and crystallographic), it is important to fully understand the fundamental concepts of the mechanism of growth. The epitaxial growth of vapor deposits has

been investigated the most, and we shall focus particularly on it. The phenomenon of epitaxy is that of a formation of a thin film with a single crystal orientation. This is usually associated with an epitaxial temperature, above which epitaxy occurs and below which epitaxy does not occur. The phenomenon is also a function of several parameters besides temperature as described elsewhere in the literature. This single crystal orientation can either be formed during the nucleation process or during the coalescence process. Concerning the formation of epitaxy during the nucleation process, there exist two extreme opinions: at one extreme there is the opinion that the particles develop an epitaxial orientation during growth which can be -but must not be- destroyed when coalescence occurs;^(6,7) at the other extreme is the view that the final orientation is determined by the most favorable orientation of critical nuclei consisting of four atoms.^(8,9,10) Several experiments by Bauer et al. give strong support to the first view.^(6,11,12) If the particles develop only one epitaxial orientation during nucleation and growth, the epitaxial orientation of the final film is then assured, provided it is not lost during coalescence. If two epitaxial orientations develop during nucleation and growth, there exists a critical stage defined by Stowell⁽¹³⁾ for which the unfavorable orientation (low interfacial energy and high surface energy) will be eliminated during coalescence and recrystallization. As pointed out by Sato,⁽⁵⁾ the problem in epitaxy is to understand the physical processes which control the orientation relationship of the deposits with respect to the crystal substrate and the degree of perfection of the final film.

The Volmer-Weber growth mode has been and still is the most

extensively studied mode of all. It corresponds to a weak interfacial interaction between deposit and substrate, which means that high surface energy predominates over the interfacial energy.

Because of that, the deposit tends to develop in three dimensions, thus avoiding the contact between the deposit and the substrate.

Depending upon the ratio of surface energy to interfacial energy, the particles will assume a specific equilibrium shape which has been studied in detail for (100) and (111) nuclei of fcc thin films.

Historically, most of the extensive studies of epitaxy are limited to the case of heteroepitaxy of metals on such ionic crystals as Au on NaCl or MoS_2 , which are typical cases of weak interfacial interaction. Since the Volmer-Weber growth mode has been widely studied, it is interesting to look at it in further detail.

In an earlier work by Pashley et al.⁽¹⁴⁾ on the epitaxial growth of gold on molybdenite by in situ electron microscopic observation, they distinguished four stages of growth process: 1) nucleation and island formation, 2) coalescence of islands, 3) channel formation, and 4) formation of the continuous film.

Two main theories were developed concerning the nucleation process: the capillarity model and the atomistic model. The capillarity theory of nucleation is based on the classical treatment of Volmer and Weber⁽¹⁵⁾ and Becker and Döring⁽¹⁶⁾ and involves such macroscopic concepts as surface energy and interfacial energy, which presuppose a fairly large size for the critical nuclei. Neglecting the interfacial interaction, Sato and Shinozaki⁽¹⁷⁾ calculated a critical size of about $8\text{-}9\text{\AA}$ at the base of the nuclei (this calculation was for epitaxial nuclei of (100) and (111) orientations on

NaCl for a deposition rate of 0.1 monolayer/sec and a substrate temperature of 400°C .) For such a small critical size, the concept of macroscopic thermodynamic properties is not applicable, and the capillarity theory does not hold.

Since macroscopic thermodynamic properties cannot be ascribed to small critical nuclei, some other concepts which involve the interfacial interaction of deposit atoms would have to be used. A model, called the atomistic model, was first proposed by Frenkel⁽¹⁸⁾ and makes use of only atomic variables. This model was further refined by Walton and coworkers.⁽¹⁹⁻²²⁾ In this atomistic theory, the critical nucleus is defined as the nucleus that contains one atom less than the smallest stable cluster, with a configuration such that the addition of a single atom in the appropriate location will produce the smallest stable cluster. In such an approach, the energy terms usually involved are the absorption energy, E_a , the surface diffusion activation energy, E_d , and the total binding energy of a group of size i , $E_b^{(i)}$. The problem is that one does not know much about E_a and $E_b^{(i)}$. It is also difficult to calculate $E_b^{(i)}$ and even worse, $E_b^{(i)}$ depends on the shape and size of the cluster. In conclusion, one has a choice between the capillarity model which ascribes macroscopic thermodynamic properties to small nuclei but gives some analytical expression of the critical size of nuclei, and the atomistic model which cannot give any prediction.

Walton et al.⁽²²⁾ circumvented the problem by using indirect method. They found that for Ag deposited on vacuum NaCl in a UHV system at a pressure of 1×10^{-9} Torr, $i^* = 1$

temperature and $i^* = 3$ at high temperature, where i^* is the number of atoms in the critical nucleus. In a usual deposition experiment, it is now generally accepted that i^* is of the order of unity.

At what stage of the nucleation should epitaxial nuclei appear? As discussed earlier, there is still some controversy on this question. Nevertheless, for fcc metals with (100) and (111) deposits, Walton⁽²³⁾ showed that the addition of one atom to a critical cluster with $i^* = 3$ forms a stable cluster with (100) orientation, and that the addition of one atom to a critical cluster with $i^* = 2$ forms a stable cluster with (111) orientation. These small stable clusters might be slightly rotated about their epitaxial orientation; but, as more and more atoms impinge on them, they tend to minimize the interfacial energy and mismatch and take the epitaxial orientation.

As the deposition proceeds, both the number and the size of the nuclei increase until these particles impinge upon each other and join together. This is now the island formation stage which is immediately followed by coalescence. Particles coalesce very rapidly in a liquid-like manner, even though they remain solid during coalescence. This was first observed by Pashley in an in situ experiment, and was interpreted by Pashley et al.⁽¹⁴⁾ in terms of sintering theory,⁽²⁴⁾ since the mass transfer is induced by capillarity and controlled by the surface self-diffusion of the deposit material. Pashley et al.⁽¹⁴⁾ explained how two particles of different orientation unite then recrystallize to form a particle with a single orientation. Nuclei with lower surface energy or high interfacial energy are then preferred over other nuclei, and complete epitaxy occurs. Stowell analyzed the

problem,⁽²⁵⁾ making the assumption that all islands are hemispherical and of uniform size. He formulated a criterion for coalescence and recrystallization in continuous and discontinuous films in term of the deposition rate, and residual vacuum. He was able to show that the critical flux of impinging atoms, which gives coalescence and recrystallization, is exponentially dependent on temperature. His treatment shows good agreement with some of the work reported in the literature.

This has been a brief resumé describing the Volmer-Weber growth mode. The reason that this mode has been studied so much is now clear. First, it involves substrates with fairly low surface energy, like the alkali halide salts, MgO , MoS_2 , etc. Most of these substrates can be easily air-cleaved or vacuum-cleaved. The formation of three dimensional nuclei in the early stage of nucleation makes it easy for them to be studied by electron microscopy. The other modes have not been studied as much because such techniques as field emission microscopy (FEM), field ion microscopy (FIM), Auger electron spectrometry (AES) or Auger spectroscopy microscopy (ASM) are required to study the early stage of deposition, since continuous layers are forming. Furthermore, because of weak interfacial interaction, the amount of mismatch tends to be larger; and any contamination of the surface (especially water vapor on NaCl) will change (increase or decrease) the interfacial energy which then might favor epitaxy. A good example is Au on NaCl .⁽²⁶⁾ Thin films of Au on air-cleaved NaCl have a high degree of epitaxy whereas epitaxy is completely lost when Au is evaporated on vacuum cleaved NaCl . This is so because the interfacial interaction of the deposits with a clean,

UHV cleaved NaCl surface is negligible and epitaxy does not occur. Recently, Vermaak and Henning⁽²⁷⁾ investigated the nature of the air-cleaved NaCl surface and found that it was mainly a hydroxide surface.

The Frank-van der Merwe growth mode has been studied the least. It corresponds to the case of strong interfacial interaction, which means that low interfacial energy controls film growth. In this mode, the deposited atoms tend to stick to the substrate, avoiding the three-dimensional buildup encountered in the Volmer-Weber mode. There is a need for a metallic substrate to produce this high interfacial interaction. Most of the epitaxial studies on metal substrates are carried out by FEM, FIM, low energy electron diffraction (LEED), which has experienced a strong revival in this field, AES, and ASM. All these techniques are ideally suited for the study of epitaxy on high melting point metals. Bauer and Poppa⁽²⁾ studied the growth of Ag and Au on W, using the LEED technique. They found that both metals have tendency to grow layer by layer at elevated temperatures, while limited surface diffusion leads to more irregular growth at lower temperatures. The concept of epitaxial nuclei does not exist in this growth mode since condensation occurs readily in a two-dimensional fashion determined by the coherence of the overgrowth and the substrate. At this stage, it is good to point out that since the existence of defects or contamination on the substrate surface is more or less unavoidable, the nature of interfacial interaction can be changed from "weak" to "strong" or vice-versa, either locally or on the substrate as a whole. This could also explain the irregular growth pattern observed at low temperatures

for Ag and Au deposited on tungsten.⁽²⁾

The last nucleation scheme that needs brief consideration is the Stranski-Krastanov mode. Bauer and Poppa found that Ag and Au on Si and Ag and Au on Cu followed this growth mode. This growth mode is characterized by a monolayer formation in the early stage of the evaporation. This is expected since the interfacial interaction is about the same as the cohesive interaction among deposit atoms. After a few layers are deposited, the deposit rearranges itself to minimize its surface energy and forms three-dimensional nuclei on top of the continuous monolayer. Such system keeps rearranging itself every time a new monolayer is added. Sometimes, the interfacial interaction is made weaker by the presence of impurities or some kind of surface disorder, and the behavior of growth can sensibly change from the Stranski-Krastanov to the Volmer-Weber type. There is more work done on this growth mode than on the Frank-van der Merwe mode, but by no means can it be compared to the Volmer-Weber case.

Most of the bcc metals studied so far exhibit polymorphic variants. Face-centered cubic structures have been obtained in ultra thin ($<100\text{\AA}$) films of tantalum and molybdenum by Denbigh and Marcus,⁽²⁸⁾ and vanadium and nickel by Bublick and Pines;⁽²⁹⁾ these convert to the normal structure as the film thickness increases. Read and Altman⁽³⁰⁾ have reported a β -phase (tetragonal) in tantalum films. Very thin films ($\sim 10\text{\AA}$) of Fe⁽³¹⁾ and Cr⁽³²⁾ were found to deposit in fcc form on metallic fcc substrates of Cu and Ni, respectively. Recently, Forssell and Persson⁽³³⁾ reported a genuine A-15 structure occurring during the growth (especially at the coalescence

stage) of thin Cr films condensed on UHV cleaved NaCl and KCl. As a matter of fact, this was an outgrowth of the work done by Kimoto and Nishida, who first reported it.⁽³⁴⁾ Finally, Sella et al.⁽³⁵⁾ observed a fcc structure for niobium films during the first stage of sputtering; they concluded that the fcc form resulted from the interaction between the metal and some residual gas present in the sputtering chamber or in the substrate surface. In general, these polymorphic variants are found in both weak and strong interfacial interactions. There is so far no reasonable explanation given for the occurrence of these polymorphic variants. Sato⁽⁵⁾ suggested that the origin must be sought in a large surface-to-volume ratio of deposited crystals.

All bcc metals listed in Table I were found to have polymorphic variants. Bond et al.⁽³⁶⁾ observed the A-15 structure in tungsten by X-ray diffraction, but could not find it when the films were examined by electron diffraction. Later, Chopra et al.⁽³⁷⁾ obtained thick and stable tungsten films with the fcc structure by the ion beam sputtering onto substrates of glass, rock salt, and mica, at a temperature of about 250-400°C. After annealing, the fcc phase transformed slowly to bcc at an annealing temperature of 700°C. In another paper, Chopra et al.⁽³⁸⁾ found the face-centered cubic modification in sputtered films of Ta, Mo, W, Re, Hf and Zr. They noted that evaporated films also assumed a fcc structure, which changed readily to the normal structure with an increase in film thickness and substrate temperature. The polymorphic variants encountered for Cr, Fe, Nb, and V were given in the previous paragraph. Table I is divided into two groups: metals with relatively

low melting point (Fe, Cr, V), and metals with high melting points (Mo, Nb, Ta, and W). Of these seven, Cr and Fe have been the most studied; but little is known about the nucleation, growth, epitaxy, and shape of the particles. So far, it seems that Cr and Fe evaporated on NaCl behave in a manner similar to that of Au on NaCl. However, there has been virtually no work done in these areas for W, Mo, Ta, V, and Nb. In general, it seems that bcc metals have a stronger tendency than fcc metals to form polymorphic variants when evaporated or sputtered onto a substrate. The reason for this phenomenon is completely unknown due to lack of experimental data for the bcc metals, especially those with high melting points.

B. Purpose of Investigation

As stressed earlier, a lot of work has been done on thin films of fcc metals, whereas very little has been done on bcc metals. Also, very little is known about the shape of the particles in bcc thin films, whereas the shapes of particles in the fcc thin films have been investigated thoroughly.

Furthermore, it would be interesting to know whether the bcc metals follow the usual Volmer-Weber growth mode when evaporated on NaCl, or whether they follow a different mode. From such a study, it could be possible to learn something about the dominant processes at the substrate surface, and to determine the reason for the formation of polymorphic variants in bcc metals.

For these following reasons, it was decided to investigate the nucleation and growth of vapor deposited tungsten on NaCl substrates. First, it would be desirable to identify the growth mode followed by tungsten on NaCl. Secondly, it is of interest to

investigate the shape of the bcc particles. Third, it is of interest to determine whether or not tungsten was present in other polymorphic variants, such as the fcc or the A-15 structure.

Finally, the results obtained for W on NaCl can be compared with those already obtained from Cr, Fe, and Nb.

II. EXPERIMENTAL PROCEDURE

A. Apparatus

All experiments done in this work were carried out in a ULTEK model TNB table top, high vacuum system fitted with a 12" X 12" pyrex bell jar with an "L" shaped Viton-A gasket. Usually, the pump down was executed in the following manner: a) the system was roughed to a pressure corresponding to about 28 inches of water, using a Bell and Gosset dry vacuum pump; b) a second roughing was then made on the system, using a cryosorption pump at liquid nitrogen temperature, lowering the pressure this time to 2×10^{-3} Torr; and c) at this stage, the titanium gettering pump was turned on, outgassed, and then the cold-cathode ion pump was turned on. Ultra high vacuum was quickly achieved by using a combination of the titanium gettering and the cold-cathode ion pump.

To achieve a high vacuum in the low 10^{-9} Torr range in a minimum of time, it was necessary to bake the system. This was easily done by turning the cooling fans off and turning the titanium gettering pump on and off every two minutes for four hours. In this way, the metal jar was heated to about 100°C , which outgassed the wall and allowed the system to be in the low 10^{-9} range ($1.5 - 2.0 \times 10^{-9}$ Torr) twelve hours later.

The pressure of the vacuum system was measured by using an automatic ranging Granville-Phillips gauge control unit, with a Bayard-Alpert ionization gauge tube.

Since it was planned to investigate the nucleation and growth of thin tungsten films by vapor deposition onto a vacuum-cleaved rock salt substrate heated to different temperatures a device was

built which would do the following: a) accept a high current for evaporation of tungsten wire, b) allow cleavage to be performed under UHV, and c) act as a substrate holder which could be heated to any desired temperature.

The apparatus for carrying out these tasks is shown in Figure 2. The main constituents are the filament holder, the cleaver-shutter, and the substrate holder. The filament holder is made of two posts (high quality molybdenum rods) firmly attached to, but isolated from, the base. The base is made of 1/4" 304 stainless steel. At one end, the two posts are connected to an electrical feedthrough by DFHC high current electrical leads. At the other end, each post has a clamp necessary to hold the tungsten filament. By passing a current through the filament, its temperature increases and, provided the current is high enough, evaporation occurs. The filament-substrate distance is about 15cm.

The substrate holder is made of a high quality, recrystallized molybdenum in order to minimize outgassing when brought to a high temperature. Such outgassing could contaminate the films during deposition. Figures 3a and 3b show a side view and a top view of the substrate holder. The four 1/4" holes observed in Figure 3a contain recrystallized alumina tubes in which tantalum wires were run. By varying the current of these wires, the substrate temperature can also be varied. This piece of molybdenum was especially machined with a cylindrical curvature of 7cm, as shown in Figure 3a. Originally, the substrate-filament distance was 7cm, but radiation was so significant that it was changed from 7cm to 15cm. All holes seen in Figure 3b are drilled to 1/8" diameter and a 3/8" depth.

These holes give enough clearance to provide a good fit for the substrate crystals. The substrates were optical grade sodium chloride crystals $1/8$ " in diameter purchased from the Harshaw Chemical Company. The substrate holder acts as a furnace for the substrate. It should be noted that the holes are arranged in seven rows.

The cleaver-shutter is mechanically driven by a direct-drive rotary motion feedthrough. The cleaver-shutter is fixed at the end of an arm, with an axis of rotation above the substrate holder and parallel to the tungsten filament. The length of the arm is the same as that of the radius of curvature of the substrate holder surface, the whole unit being slightly deplaced upwards such that the cleaver-shutter executes a smooth motion $1/4$ " above the substrate holder surface when the direct-drive mechanism is actuated. Hence, any substrate rods extending more than $1/4$ " above the substrate holder surface are cleaved by the motion of the cleaver, thus producing a vacuum-cleaved surface.

The advantages of such a system are numerous. The substrate holder, being heavy, does not "feel" much of the effect of radiation for a short evaporation time, thus keeping a constant substrate temperature. Since the substrate holder acts as a furnace, the deposition can be performed at different substrate temperatures. Several thin films can be produced for each run; and, most important of all, a gradient in thickness can be produced by successively masking off the rows using the cleaver-shutter. For example, it is possible to get thin films having the following evaporation times: 5, 10, 15, 20, 25, 30, and 35 minutes. Provided the evaporation rate is correctly chosen, these evaporation times can cover the whole

range from the early nucleation stage to the final coalescence stage, which enables a good study of the nucleation and growth process.

However, the present system also possesses some disadvantages. A long time is needed to bring and stabilize the substrates to the required temperature. Of course, this is due to the large mass of the substrate holder. Furthermore, the substrates require a long time to cool down because of the massive holder. For high substrate temperatures, this means that atomic rearrangement can still occur after evaporation is stopped. Since the substrate rods are cantilevered they cleaved at different heights with respect to the baseplate. Sometimes, they cleaved below the substrate holder surface, and these films had to be discarded. Also, the top of freshly cleaved substrates sometimes fall on other freshly cleaved substrates; such crystals were rejected. Due to the position of the substrates rods, debris sometimes remains on the surface after cleavage. The high density of debris can occasionally change the nature of the film.

To provide the necessary current for the source and the furnace, two different power supplies were built. The power supply for the source consists of a 30 amp variac whose output is stepped down by two transformers to give the necessary current (0-100 amps) to evaporate the tungsten wire. A similar power supply was built using a 10 amp variac and one transformer having an output capability of 50 amps. This current was enough to heat the substrate to a temperature of 500°C . These two variacs were driven by a Sola constant voltage transformer to provide reasonable regulation of the

filament and the substrate temperatures.

The last piece of equipment used in the present experiments was a chart recorder displaying a continuous readout of the substrate temperature. As shown in Figure 3b, the temperature was measured in the middle of the substrate surface holder by the use of an alumel-chromel thermocouple.

B. Evaporation Rate

The problem encountered was not of measuring the evaporation rate, but rather of obtaining a constant evaporation rate. By a very simple argument, Langmuir et al.⁽³⁹⁾ arrived at the relation

$$V'^3 \sqrt{A'} = \frac{V^3 \sqrt{A}}{l}$$

where V is the potential drop over the filament measured in volts, A is the filament heating current expressed in amperes, and l is the length of the filament. The primed quantities are called specific characteristics of the filament. These functions are independent of the dimensions of the filament, but do depend on its temperature. For a given value of A' or V' , the temperature of the filament can be determined by using the value tabulated by Langmuir et al.

To maintain the filament at a constant temperature, one should maintain

$$\frac{V^3 \sqrt{A}}{l} = \text{constant}$$

even when the diameter changes considerably. This gives a fairly constant evaporation rate, assuming that l is fixed and that the diameter does not change too much (less than 5%), which is indeed the case in the present experiments.

However, the Langmuir calculations are based on an "ideal

filament" which is assumed to be a very long, straight filament of uniform, circular cross-section, thoroughly aged, consisting of pure tungsten with a definite specific resistance at a given temperature, and possessing a bright, clean surface.

By using a filament of 8cm length, this first assumption is surely met. Also, all filaments used in the experiments were aged at 2500°K for two hours which also satisfies the second assumption. The purity condition is also met, since the tungsten used is of a VP grade (Materials Research Corporation). In general, the condition of an "ideal filament" exists, and the relation $(V^3 \sqrt{A})/l$ holds.

The relation between filament current and deposition rate was determined empirically. Originally, it was desired to work with an evaporation rate on the order of $0.01\text{\AA}/\text{sec}$. But due to a low sticking coefficient of tungsten on rock salt in the early nucleation stage, it appeared that contamination was playing an important factor and consistent results were not obtained. A higher rate of $0.035\text{\AA}/\text{sec}$ was then used. The current corresponding to such an evaporation rate was determined the following way. Since a film layer of $300\text{\AA}$ can be determined accurately using a 2-beam interferometer, it was decided to prepare films with such thickness. To obtain a $300\text{\AA}$ film at a rate of $0.035\text{\AA}/\text{sec}$, it takes about 2 hours and 23 minutes. A microslide which already had a layer of tungsten on its surface was half-masked and put in the vacuum system for evaporation. Then several similar experiments were performed, using different filament currents but, keeping the evaporation time (2 hours and 23 minutes) constant. Then calculation of the height of the step on the microslide gave the required information. Several

experiments were performed later on, and they all were very consistent, which verifies the assumption of an "ideal filament."

C. Type of Experiment

All experiments were performed at a constant evaporation rate of $0.035\text{\AA}/\text{sec}$. The substrate temperatures used were 25, 150, 250, 350, and 450°C . Some experiments were also done on air-cleaved NaCl, using the same temperatures as above. A comparative run was made using vacuum-cleaved KCl with a substrate temperature of 350°C .

The tungsten filament used was a 0.015" diameter wire, of VP grade (99.97%), purchased from the Material Research Corporation.

D. Typical Runs

All experiments were carried out with pressures in the low 10^{-9} Torr range. First, the substrate was heated to the desired temperature, stabilized and held there for two hours prior to deposition. The next stage was to slowly bring the tungsten filament to the required temperature (3200°K for $0.035\text{\AA}/\text{sec}$). This was immediately followed by a cleavage of all substrate rods by a quick motion of the cleaver-shutter, exposing the freshly cleaved surface to the stream of tungsten vapor. During the runs, three parameters had to be changed: voltage across the filament, the thickness gradient, and the substrate temperature.

In order to keep a constant evaporation rate, the temperature of the filament had to be kept constant. This was readily done by keeping $(V^3 \sqrt{I})/\ell$ constant. So the procedure was the following. The parameter ℓ is fixed by the configuration of the system. I_0 and V_0 are read at the beginning of the evaporation process; then the constant $(V^3 \sqrt{I/\ell})$ is calculated. Given a value for I , the

corresponding value for V is readily obtained from the equation $V^3 \sqrt{I/\rho} = \text{constant}$. By trial and error, it was found that change needed to be made any time the current was decreased by 0.25 amp. Using a programmable calculator, the values of V_i , corresponding to $I_{i+1} = I_i - 0.25$ amp were calculated. As the evaporation proceeded, the characteristics of the filament changed and so did the current and voltage. Every time the current dropped by 0.25 amp, the voltage was adjusted correspondingly, thus keeping the temperature and the evaporation rate of the filament constant.

The thickness gradient was not difficult to control and was obtained by masking off the rows, one after the other, after a given evaporation time. Usually, a row was masked off every five minutes. This was done by rotating the cleaver-shutter.

The substrate temperature was continuously recorded on a chart recorder. Since the temperature of the substrate holder tended to increase (especially at low temperatures) due to radiation, the current of the furnace was lowered once in a while to keep the substrate temperature constant. However, a rise of 20°C was usually observed at room temperature, and this could not be avoided. Even though the temperature of the substrate holder was kept constant in most experiments, this does not mean that the substrate temperature was kept constant. It would be important to know more about the substrate surface temperature in such experiments where radiation is important.

When the evaporation was over, the substrate was slowly cooled to room temperature (for a substrate at 350°C , it takes a day to cool to room temperature). The vacuum system was opened and the

specimens removed. They were then placed in a diffusion pumped vacuum system (10^{-6} Torr) to be backed with carbon by evaporation. The films were floated off the substrate in distilled water and scooped up onto a 400 mesh copper grid.

Using a Hitachi HU-11B-3 and a Hitachi HU-12, the tungsten films were examined by transmission electron microscopy (bright and dark field) and diffraction. Some high resolution diffraction patterns were obtained for a few films using the Hitachi HU-11B-3.

III. RESULTS

A. Vacuum-Cleaved NaCl

1. Substrate at 350°C

The general sequence of nucleation and growth of films where the substrate was maintained at 350°C two hours prior to and during evaporation is shown in Figures 4a-g. The shortest evaporation time observed was five minutes which then increased up to thirty-five minutes in steps of five minutes. The processes studied in the present work were nucleation, growth, and coalescence. According to an arbitrary classification, based on the results of Figures 4a-g, one can further divide these processes in the following way: nucleation (Figures 4a and b), star-like formation (Figure 4c), dendritic growth (Figures 4d-f), and coalescence of the nuclei (Figure 4g).

It should be noted that this arbitrary classification applies only to thin tungsten films evaporated onto a vacuum-cleaved (hereafter designated VC) NaCl substrate at 350°C. The reason for introducing such a classification is to simplify the interpretation and description of the results.

a. 5 minutes

For a short evaporation time (five minutes) the particles are rather small and faint. Preferential nucleation along steps and defects is observed as shown in Figure 4a. Since the particles are small, it is difficult to obtain good micrographs for such thin films. The best results were obtained when focusing was done on the carbon support film (about 100Å thick) rather than on the tungsten particles. At a magnification of 100K or higher, one can observe the granular image of the carbon film changing with focus. At an underfocus of

about $600\text{\AA}$, granules of specific size are visible in reasonable contrast and this is considered to give the most faithful image. Figures 4a-g are examples of this focusing technique.

In the wide-area diffraction pattern, Figure 5a (which corresponds to Figure 4a) one can observe two distinct halos (broadened Debye rings). The s -values of these are respectively $1.2\text{\AA}^{-1}$ for the inner halo and about $2.9\text{\AA}^{-1}$ for the outer one, s being $(4\pi/\lambda) \sin\phi$, where λ is the wave-length of the electrons and 2ϕ is the scattering angle. In fact, Kakinoki et al.⁽⁴⁰⁾ studied the structure of such carbon films by electron diffraction using a camera with a rotating sector and found up to eleven halos or maxima. Table II is a summary of Kakinoki's results for carbon and some of the calculated s -values corresponding to the (hkl) planes of tungsten. From this table, there is no doubt that the two observed halos are due to the carbon film. However, the second maximum from carbon and the (110) ring of tungsten have very close s -values, i.e., $2.9\text{\AA}^{-1}$ for carbon and $2.8\text{\AA}^{-1}$ for tungsten. Since the very thin tungsten films are mainly amorphous, the (110) ring is expected to be broad; the fact that the s -values are close makes it difficult to confirm whether or not the tungsten film is contributing to the second maximum.

b. 10 minutes

As the evaporation time increases, the particles grow larger in size, their density increases, and preferential nucleation along steps becomes more prominent as shown in Figure 4b. The wide-area diffraction pattern corresponding to Figure 4b is displayed in Figure 5b. One can observe a strong inner halo, a weak middle one,

and a reasonably strong outer one. The calculated s -values are $s = 2.8\text{\AA}^{-1}$ for the inner halo, $s = 4.0\text{\AA}^{-1}$ for the middle one, and $s = 5.5\text{\AA}^{-1}$ for the outer one. From Table II, the inner and outer halos correspond respectively to the second and third maxima of carbon, whereas the weak halo in the middle corresponds to the (200) ring of tungsten. In order to show these three halos simultaneously, some skill had to be used during the printing process. The center part was over-exposed whereas the remaining part was under-exposed in both Figures 5a and 5b. Of course, the relative intensities of the halos are lost. On the original electron micrograph, the relative intensities are as follow: the inner ring has very strong intensity, the middle one is rather weak, and the outer one has medium intensity. The strong intensity of the first halo is again attributed to the contribution of the second maximum of carbon, with $s = 2.9\text{\AA}^{-1}$, plus the diffuse (110) ring of tungsten, with $s = 2.8\text{\AA}^{-1}$. The diffuseness of the (110) and (200) rings is a characteristic of the fine grained (grain size of about $10\text{-}20\text{\AA}$) structure^(41,42) commonly obtained in covalent and high melting point materials. Calculation of the density gives about 1.5×10^{11} nuclei/cm²; however, this number is not too reliable because of a high density of substrate steps. A lower figure would then be expected since the density of nuclei is much higher along steps than on a "flat" surface.

c. 15 minutes

The electron micrograph of Figure 4c reveals three main types of particles: square, star-like, and "noncrystallographic" particles. Their mean diameter varies from 100 to $150\text{\AA}$. In this work, the star-like particles are defined as those having a star-like shape,

but with only four arms being 90° apart from each other. Particle A of Figure 4c is a good example of a star-like particle. On the other hand, all particles, crystalline or not, with a random orientation and no specific external shape (or faceting) are classified as noncrystallographic. Fukano and Wayman^(43,44) observed such square and star-like particles for chromium on both NaCl and graphite substrates. Lewis and Stirland⁽⁴⁵⁾ obtained similar particle shapes by evaporating lead telluride on vacuum-cleaved NaCl at 100°C . The average thickness of their film was about $72\text{\AA}$, which is twice the thickness of the film shown in Figure 4c. The wide-area diffraction pattern corresponding to Figure 4c is given in Figure 5c, and shows a polycrystalline texture (hereafter designated PCT) with a (100) preferred orientation. The orientation relationship between the tungsten film and the substrate is

$$\{100\} \langle 110 \rangle \text{ W } // \{100\} \langle 100 \rangle \text{ NaCl.}$$

A dark field image taken with a (110) spot showed that (90% of cases) the square and star-like particles are mainly epitaxial.

In the previous paragraph, the particles observed in Figure 4c were classified with respect to their shapes. However, there are still other particles which are neither square nor star-like in shape, but which possess a specific symmetry and orientation relationship with the substrate. For example, particle B in Figure 4c has a three-fold symmetry, and particle C, whose shape resembles an X, has a two-fold symmetry about a $\langle 100 \rangle$ direction of the substrate surface.

At this stage, it is good to point out that the morphology of the various films was found to vary considerably, not only from

run to run, but also from specimen to specimen, and even worse, from different areas of the same specimen. This was observed by transmission electron microscopy and diffraction. In some cases, the diffraction pattern, upon sweeping the specimen across the beam, was observed to change from that of a PCT to that of a bcc texture plus an unknown structure. Both a change in the shape of the particles and a drastic change in their density were observed as can be seen in the sequence of electron micrographs in Figure 6. The first tempting rationalization is to relate such inconsistency to the various parameters involved during evaporation or film preparation (backing the films with carbon and floating them off in distilled water). But in all experiments care was taken to keep such parameters consistent. The experiments were all performed under high vacuum (always less than 2×10^{-8} Torr), the substrate temperature was kept very close to its intended value during the evaporation process (except at room temperature), and finally, all filaments were aged at the same temperature for the same time. However, in some cases, there was no doubt that some of the W-particles were detached from the carbon-backing during the floating process; this could be easily observed on the carbon replica. Note that in the sequence of electron micrographs of Figure 6, no evidence is observable for the loss of some particles during the floating process.

The growth mode illustrated in Figure 4a-g was selected for analysis compared to the different mode observed in Figures 6a for the following reasons: a) this mode was dominant and observed in all experiments, b) it exhibited some interesting crystallographic variants, and c) it leads to a study of the shape and orientation of

the deposits of tungsten thin films.

d. 20 minutes

This stage of the growth process, displayed in Figure 4d, is characterized by further growth of the star-like and noncrystallographic particles. The number of particles having an X-shape is also more appreciable. The particle density is about 5×10^{10} nuclei/cm² and the average diameter is about 500Å. In the interval between Figure 4c and Figure 4d, dendritic growth has started. As observed in Figure 4d, dendritic growth occurs at a much faster rate for the X-shape and noncrystallographic particles than for the star-like particles.

The wide-area high resolution diffraction pattern, Figure 5d, shows that arcing is present in all the α -W Debye rings, thus indicating that a single preferred orientation does not exist. Furthermore, a two-fold symmetry about the {100} orientation of the main {100} texture is indicated by the arcs in the (210), (310), (222), and (321) rings. An attempt was made to index this diffraction pattern. The main orientations were found, but there still remained a number of arcs that could not be satisfactorily explained. The listing below gives these main orientations and a schematic showing the relationship between these orientations and the substrate is given in Figure 7.

- a) {100} <110> W // {100} <100> NaCl
- b) {100} <100> W // {100} <100> NaCl
- c) {110} <001> W // {100} <100> NaCl
- d) {123} W // {100} NaCl

The first PCT with a (100) preferred orientation is the

In the wide-area diffraction pattern, Figure 5e, the (100) texture is still predominant; there is practically no trace of the other texture. Three new rings appear, close to the (100) ring of the bcc structure. One of them is nearly superimposed on the (110) bcc ring, one is inside the (110) ring, and the last is outside the (110) ring. There are also many other weak rings beyond the (200) ring of the bcc structure. These additional rings may be caused by polymorphic variants of tungsten. Thus far, two polymorphic forms have been observed for tungsten thin films: a) a fcc structure with $a = 4.15\text{\AA}$, first observed by Chopra et al.,^(37,38) and later by Miska and Gillet,⁽⁴⁶⁾ and Sella and Coppens,⁽⁴⁷⁾ b) an A-15 structure with $a = 5.036\text{\AA}$, first observed by Bond et al.⁽³⁶⁾ and then by Basavaiah and Pollack.⁽⁴⁸⁾ The presence of these three closely spaced rings and their relative position with respect to the (110) ring of the bcc structure indicate the occurrence of the A-15 structure. More rings with substantial intensity are needed to properly index this new phase.

f. 30 minutes

Dendritic growth and coalescence are the prevailing processes for this evaporation time (Figure 4f). Whereas particles growth is maximum, the coalescence process is just starting. The diameter of the particles has increased from about $500\text{\AA}$ to $750\text{\AA}$, but the particle density remains sensibly the same ($4 \times 10^{10}/\text{cm}^2$) as for the 25 minute evaporation time.

The wide-area diffraction pattern, Figure 5f, clearly shows the presence of both the bcc and A-15 structures. Figure 9 is an enlargement of 4f in which one half was overexposed and the other

half underexposed. With this technique, all rings for the bcc and A-15 structures can be observed simultaneously. Using the same technique for Figure 10, all the rings of the A-15 structure can be indexed. The (210), (421), and (600) rings of the A-15 structure superimpose respectively on the (110), (220), and the (321) rings of the bcc structure.

The α -W (bcc) particles have the same preferred orientation as described in Figure 7. On the other hand, the β -W (A-15) particles also exhibit PCT's with preferred orientations. The main textures, classified by decreasing order of importance (as determined by intensity), are given below with their respective orientation relationships.

- a) $\{001\} \langle 110 \rangle \beta\text{-W} // \{001\} \langle 100 \rangle \text{NaCl}$
- b) $\{011\} \langle 100 \rangle \beta\text{-W} // \{001\} \langle 100 \rangle \text{NaCl}$
- c) $\{001\} \langle 100 \rangle \beta\text{-W} // \{001\} \langle 100 \rangle \text{NaCl}$

It should be noted that the preferred orientations for the β -W are exactly the same as those for α -W, and also arranged in the same order regarding the intensity.

g. 35 minutes

This evaporation time, which corresponds to an advanced stage of coalescence, was the last studied. At this stage most of the particles impinge and the interparticle regions are filled by further growth. Recrystallization also occurs, and the star-like particles change into flower-like particles, resembling the noncrystallographic particles.

The wide-area diffraction pattern, Figure 5g, is interesting. The α - and β -W phases have now disappeared and a new fcc phase has

appeared. The lattice spacing for this fcc structure is about $4.25\text{\AA}$, which is 2.5% off the value measured by Chopra et al. (37).

The round shape of the particles in Figure 4g indicates that surface energy plays an important role in stabilizing this new fcc phase. Thus, at 350°C , the coalescence stage is characterized by the elimination of the α - and β -W phase and the appearance of an fcc phase with a weak PCT.

2. Substrates at 250 and 150°C

For films deposited on vacuum-cleaved substrates (hereafter designated VCS) at 250 and 150°C , the early stages of nucleation and growth are of the Stranski-Krastanov (hereafter designated SK) type which then changes to the Volmer-Weber (hereafter designated VW) type as the thickness of the film increases. The results are thus different from the 350°C case. The degree of PCT increases with substrate temperature. Furthermore, the α - and β -W variants are observed for both 150 and 250°C films.

a. 15 minutes

The bright field electron micrograph, Figure 11a and 11d, which correspond respectively to films grown on 150 and 250°C substrates, show thin continuous tungsten films in which three-dimensional particles are imbedded. This is characteristic of the SK growth mode. In some cases, parts of the film were detached during the floating process and gave a light contrast under bright field microscopy. This was interpreted as direct evidence for a continuous thin tungsten film rather than a continuous thin contaminant film. The wide-area diffraction patterns, Figures 13a and 13b, which correspond respectively to 150 and 250°C , show only a broad

ring. Note that this broad (110) α -W ring is characteristic of small grain size particles. (41,42)

b. 25 minutes

In going from 15 to 25 minutes, the films have changed from continuous to three-dimensional particles as shown in Figures 11b (150°C) and 11e (250°C). Whereas films obtained at 150°C show only noncrystallographic particles which give a weak (100) texture, films obtained at 250°C show many star-like particles which give a strong (100) texture (Figure 12e). The substrate temperature affects then the morphology of the tungsten particles and thus the degree of epitaxy of the film.

c. 35 minutes

The bright field images, Figures 11c (150°C) and 11f (250°C), show an increase in particle size and predominance of the dendritic growth. The corresponding wide-area diffraction patterns, Figure 12c and 12f, show a (100) texture for both the α - and β -W variants. Again, films obtained at 250°C exhibit a larger particle size and more developed morphology and consequently a higher degree of epitaxy than films obtained at 150°C.

3. Substrate at 25°C.

Three successive evaporation times, 15, 25, and 35 minutes, were investigated for tungsten films grown on VC NaCl at 25°C. In the early stages of deposition, the growth mode is of the SK type, which then changes sluggishly to the VW type as the thickness of the film increases. The growth behavior at 25°C is thus similar to that at 150 and 250°C. Both phases, the α - and β -W, are present on VC NaCl at 25°C.

a. 15 minutes

The bright field electron micrograph and the wide-area diffraction pattern for such an evaporation time are displayed respectively in Figures 13a and 13d. The bright field image shows a thin continuous film of tungsten with three-dimensional particles, which is characteristic of the SK growth. The diffraction pattern shows a broad (110) α -W ring.

b. 25 minutes

In going from 15 to 25 minutes, the film appears to have rearranged from the SK to VW modes. The film of Figure 13b shows three-dimensional noncrystallographic particles. Note that the film is in an advanced stage of coalescence. The wide-area diffraction pattern, Figure 13e, shows a weak (100) texture for the α -W phase.

c. 35 minutes

The film, which is displayed in Figure 13c, has now completed the coalescence stage and is in the necking stage. Some of the particles are large crystallites exhibiting exceptionally good contrast; a few of them show faceting along the $\langle 100 \rangle$ directions of the substrate surface. The wide-area diffraction pattern, Figure 13f, indicated the presence of both α - and β -W. Whereas α -W shows a weak (100) texture, the β -W is completely polycrystalline.

4. Substrate at 450°C

Clarke and Czenderna⁽⁴⁹⁾ used a vacuum microbalance to measure the mass loss of (100) cleaved NaCl during thermal etching in a vacuum of 5×10^{-7} Torr or better. The sublimation rates for cleaved NaCl are given in Table III for different temperatures. In these calculations, they assumed a roughness factor of unity.

From the experiments carried out at 25, 150, 250, and 350°C, the degree of epitaxy was observed to increase with temperature. It was thus of interest to determine if high quality epitaxial films could be grown at 450°C. From Table III, 4.5 monolayers would sublime during an evaporation time of 35 minutes at 350°C; however, the effect of such sublimation rate on the nucleation and growth of tungsten thin films is not known.

Thus a run was made on VC NaCl at 450°C. Noticeable particles were not observed before an evaporation time of 30 minutes. The best tungsten films, with a relatively high density of nuclei, were obtained after 35 minutes of evaporation; an example is given in Figure 14a. However, the results were inconsistent: some areas were similar to Figure 14a, and others did not show any tungsten particles. For a long evaporation time, the effect of the NaCl sublimation is easily observed. As the steps sublime, they deplete the "flat" surface of tungsten particles. These particles are trapped at the steps, agglomerate, and form elongated islands of particles which then break away from the steps as their mass becomes too large. These elongated particles, which are more or less arranged in parallel, can be seen in Figure 14b. Both wide-area diffraction patterns, Figures 14c and 14d, show that the particles are polycrystalline α -W; there is no trace of the β -W.

5. KCl Substrate at 350°C.

Several experiments were performed on VC NaCl with the substrate temperature ranging from 25 to 350°C. In most cases, the α -W phase was always weakly present, so satisfactory dark field work could not be done to identify the presence and the shapes of the β -W

particles. For the best case considered, that is for tungsten films condensed on VC NaCl at 350°C, a dark field image taken with a (200) β -W spot showed only small amorphous particles.

Persson and Forssell⁽³³⁾ studied Cr on both NaCl and KCl substrates, and observed that no discrete particles of the β structure were formed in Cr films condensed on NaCl; however, some were formed on KCl. Since W films condensed on NaCl showed amorphous nuclei, it was of interest to determine if tungsten films condensed on KCl would follow a pattern similar to Cr films. Thus, one could possibly investigate the shapes of nuclei for the β structure.

The results obtained are shown in the sequence of electron micrographs of Figure 15. Figure 15a is a bright field image of a tungsten film of average thickness 52Å. Comparing Figure 4d (VC NaCl at 350°C) with Figure 15c (VC KCl at 350°C), the particle morphology is about the same, except for the complete absence of dendritic growth on KCl. The wide-area diffraction pattern, Figure 15b, is properly oriented with respect to the bright field image of Figure 15a and the dark field image of Figure 15c and 15d. The dark field image of Figure 15c is taken with a (110) spot of the α -W phase whereas that of Figure 15d is from a (200) spot of the β -W phase. Since the (200), (210), and (211) rings of the β -W and the (110) of the α -W are very close, contribution from more than 1, 2, or 3 rings could not be eliminated during dark field work, due to the physical size of the objective aperture (20 μ).

In the bright field image of Figure 15a, one can recognize star-like particles (A), X-shape particles (B), and several particles having a three-fold symmetry (C) besides the noncrystallographic

particles. These particles all belong to the α -W variant. The dark field image taken with a (110) α -W spot, Figure 15b, reveals that the star-like particles have the (100) orientation; however, nothing can be said about the X-shape particles.

Concerning the shape of the β -W particles, most of the particles do not have any discrete shape except a few, as indicated in the dark field image taken with a (200) spot. For example, the particles, indicated by F, have a clear rectangular shape and are indeed (100) β -W nuclei. Other particles, indicated by E, have a kind of rhomboid shape and belong to (110) nuclei. Note that the rectangular and rounded rhomboid shapes have been observed by Persson and Forssell⁽³³⁾ and Kimoto and Nukida⁽³⁴⁾ for Cr on NaCl.

B. Air-Cleaved, Preheated NaCl

Green and Bauer⁽⁵⁰⁾ noted that NaCl crystals exposed to atmospheric pressure (~38% relative humidity) for only a few minutes after cleavage show only a gradual increase over the background H₂O peak when heated to high temperatures in a high vacuum system. Harsdorff⁽⁵¹⁾ reported that the water desorbed during exposure to the atmosphere is removed layer-by-layer when NaCl single crystals are heated in vacuum. Later observations of Harsdorff⁽⁵²⁾ suggest that absorbed gases influence the structure of evaporated fcc metal films unless the NaCl is heated in vacuum to above 450°C before the metal is deposited. The high temperature bakeout (500°C for several hours) used by Blatz⁽⁵³⁾ to "clean" NaCl surfaces did indeed remove some contaminants absorbed during exposure to air.

Matthews and Grunbaum⁽⁵⁴⁾ used a NaCl crystal and exposed it to air at atmospheric pressure for one hour, then heated it to 450°C

in UHV for 2 hours, cooled it to 360°C and coated it with gold at $10\text{\AA}/\text{sec}$. The film obtained was undistinguishable from those grown on freshly cleaved substrates. Henning⁽⁵⁵⁾ used thermally etched specimens to study the growth of gold films on NaCl in high vacuum. He observed that a preheat treatment at 500°C for 10 minutes does not always give a clean surface. Patrician and Wayman⁽⁵⁶⁾ compared thermally etched air-cleaved NaCl (hereafter designated AC) with VC NaCl substrates. Some specimens were AC, heated to 450°C for 8 hours, and then cooled to 350°C for evaporation. The films prepared this way were similar to films deposited on VCS except for the number of cleavage steps. All small steps were removed in the preheat treatment. The only difference was in the number of the nucleation sites.

In light of these results, it appears possible to obtain a clean surface comparable to a VC surface, provided a suitable preheat treatment is used. The preheat treatment used in the present case was the following: specimens were thermally etched at 500°C for 30 minutes and cooled to the desired substrate temperature for about 30 minutes prior to evaporation. The reason that 30 minutes was used for both the etching and cool down time is that the surface takes 15 minutes to reach the equilibrium temperature according to Clarke and Czanderna.⁽⁴⁹⁾ Assuming that the surface does indeed take 15 minutes to reach the equilibrium temperature, it is implied that the specimen is thermally etched for about 15 minutes. Thus excessive preheat treatment is avoided and accordingly fewer small steps are removed, giving then a surface morphology close to that of a VC surface. Similarly, for the cool-down process, 30 minutes were sufficient for the surface temperature to reach equilibrium.

1. Substrate at 350°C

Only three evaporation times (10, 15, 25 minutes) were investigated for tungsten films evaporated onto AC NaCl substrates with preheat treatment. The nucleation process is characterized by a very high density of nuclei, in agreement with the results of Matthews and Grunbaum⁽⁵⁴⁾ for gold films evaporated onto AC NaCl substrates with similar preheat treatment. A very weak (100) texture persists during nucleation, growth, and the coalescence process. The β -W structure is also present.

a. 10 minutes

On air-cleaved, preheated substrates (hereafter designated ACPS), the early stages of nucleation and growth are of the VW type as shown in Figure 16a. The steps are heavily decorated and the particle density (3×10^{11} nuclei/cm²) is about an order of magnitude higher than on VCS (5×10^{10} nuclei/cm²) at the same temperature. The particles are small (100-200Å) and noncrystallographic. The wide-area diffraction pattern displayed in Figure 16d shows a very weak (100) texture for the α -W phase.

b. 15 minutes

The electron micrograph and wide-area diffraction pattern of such a film are displayed respectively in Figures 16b and 16e. Not much growth occurred between 10 and 15 minutes; however a few star-like particles are observed at 15 minutes and are indicated by an arrow in Figure 16b. The wide-area diffraction pattern still shows a (100) α -W texture and broad Debye ring inside the (110) spots. This broad ring is probably the (210) ring of the β -W phase and is due to the small particle size of this phase.

c. 25 minutes

The few star-like particles observed at 15 minutes are now completely gone as indicated in Figure 16c. The particles, all noncrystallographic, impinge upon each other, coalesce and form a kind of flower-like arrangement with an average diameter of $500\text{\AA}$. The wide-area diffraction pattern, Figure 16f, again shows a very weak (100) texture for the α -W phase and some broad rings corresponding to the β -W structure.

2. Substrate at 25°C

At this temperature, the initial nucleation and growth processes of films evaporated on ACPS are different from those of films evaporated on VCS. The etching process did not completely remove all contaminants on the ACPS. The substrate-deposit interaction was thus screened by the presence of contaminants and a different growth mode occurred. As the evaporation time increased, the film rearranged and three-dimensional noncrystallographic particles formed. The β -W structure was also observed at this substrate temperature.

a. 10 minutes

As shown in Figure 17a, two growth modes prevail for such an evaporation time: the VW mode (three-dimensional particles) and the SK mode (areas having a thin continuous film). The wide-area diffraction pattern, Figure 17d, shows a very broad (100) α -W ring.

b. 15 minutes

A rearrangement from the SK to the VW mode took place as revealed by the electron micrograph of Figure 17b. The three-dimensional particles resulting from this change are noncrystallogra-

phic. The wide-area diffraction pattern, figure 17e, shows again a broad (110) α -W ring, emphasizing the amorphous nature of the particles and their small grain size.

c. 20 minutes

No significant change was observed between 15 and 20 minutes. Some new particles nucleated and grew, and the average particle size increased, as shown in figure 17c. The wide-area diffraction pattern figure 17f, shows the presence of both the α - and β -W phase. Note that both phases are completely polycrystalline. Two tungsten films, having an average film thickness of 100 and 150 Å, were evaporated on ACPs at 25°C. The purpose of such an experiment was first to measure the lattice spacing of tungsten thin film compared to the bulk value and secondly, to observe the effect of film thickness on the film itself. The high resolution diffraction patterns for these two films are given in figures 18a and 18b. The calculated lattice spacing for the tungsten films is about 3.12 Å, which is less, but not much, than the bulk value, 3.158 Å. The effect of thickness is to obscure the PCT as the thickness increases. The (100) PCT of figure 18a, which is partially obscured, becomes totally obscured as the thickness increases, figure 18b.

IV. DISCUSSION

A. Growth Modes

The growth mode of tungsten films evaporated onto VC NaCl at 350°C is of the VW type, as shown in Figure 4a-g. At lower substrate temperatures, 25, 150 and 250°C, the initial growth modes is of the SK type, at least up to a certain film thickness, after which a transition from the SK to VW mode occurs. At an average film thickness of 32Å, the films shown in Figures 11d, 11a, and 13a (which correspond respectively to substrate temperatures of 25, 150, and 250°C) exhibit the SK mode. However, when the film thickness has increased to 52Å, only the VW type of growth occurs (Figures 11e, 11b, and 13b).

At 250, 150, and 25°C, the formation of α -W films on VCS occurs in the following way. In the early stages, very thin islands of noncrystallographic shape are formed; these have a large width to thickness ratio. These islands grow rapidly and soon coalesce to form a continuous film. As the (continuous) film thickness increases, evidently elastic strains are built up to the point where the film becomes unstable and breaks up into three dimensional islands. Further growth then occurs by the enlargement of these clusters. Since thin continuous layers are not formed (again) between the clusters, it would appear that contamination of the substrate has reduced the substrate-deposit interaction, thus giving rise to the type of growth observed at the later stages.

Since films grown on VCS at 350°C were the most thoroughly investigated, a brief discussion of the growth mechanism for these is given. As shown in Figure 4a-g, nucleation involved the formation

of very small particles of different orientations relative to the substrate. It is possible that more than one type of particle exists at this stage. Because of a strong substrate-deposit interaction, the well-oriented nuclei are believed to be pseudomorphic in the early stages. However, as they grow, misfit strains increase and a possible loss of initial orientation can occur. Some evidence indicating the importance of misfit strains has been obtained, particularly for the case of films on VCS below 350°C , but it should be noted that the well-oriented star-like particles can grow to appreciable size without "breaking up."

In the early stages of deposition, when contamination is still low, the star-like particles grow rapidly since misfit dislocations can be generated at the particle-substrate junction to decrease the elastic strain. Because of the well-defined crystallographic requirements for dislocations, such a process may not apply to the noncrystallographic particles in a random orientation with respect to the substrate. Presumably, the noncrystallographic particles grow freely because contaminants screen the effects of the substrate potential. While these particles are growing, a secondary growth which is dendritic in appearance (but not actually dendritic) forms on the star-like particles and impedes their further growth. This discussion explains the results observed in Figure 4a-g.

Initially, the star-like particles overwhelm the noncrystallographic particles and give rise to strong PCT's as observed in Figure 4a-d. But, as contaminant layers build up on the surface, the growth of the noncrystallographic particles increases, and also new noncrystallographic particles nucleate. Finally, the

noncrystallographic particles overwhelm (in size and in number) the star-like particles and the film appears polycrystalline; only Debye rings are seen in the diffraction patterns.

The growth mode of films evaporated on ACPS is similar to that observed on VCS. The only difference found is at 25°C. Thin continuous films are not observed to form in the early process of evaporation on ACPS. A possible explanation for this is that a reduction in the substrate-deposit interaction occurs due to contaminants which were not effectively removed by the thermal etching process.

Though the modes of film growth do not differ too much when comparing VCS and ACPS, the films do differ somewhat in the observed particle morphology and in the degree of epitaxy. For films obtained on VCS, the number of crystallite particles and the degree of epitaxy increase as the temperature increases (compare Figures 4a-g and 5a-g (350°C) with Figures 13a-c and 13d-f (25°C)). On the other hand, films obtained on ACPS consist mainly of noncrystallographic particles with a very weak PCT (Figure 16a-f and 17a-f). The main difference then is that VCS lead to partial epitaxy whereas ACPS lead to completely polycrystalline films.

B. Polymorphic Variants

Tungsten is known to have two forms: the α -W structure (bcc) and the β -W structure (unit cell of A-15 type and space group O_h^3 - Pm3n). The β -structure in bulk tungsten was first reported by Hartman et al.⁽⁵⁷⁾ in 1931 who calculated the lattice constant to be 5.036 Å. Later on, Bond et al.⁽³⁶⁾ and Basavaiah and Pollack^(48,58) observed the β -W structure respectively in thick and thin tungsten

films. Recently, Chopra et al.^(37,38) reported a fcc structure for thin tungsten films. This fcc phase was also obtained by Sella and Coppens⁽⁴⁷⁾ and Miska and Gillet⁽⁴⁶⁾ using different evaporation techniques. For simplicity, the fcc tungsten structure will be designated by the Greek letter γ . Tungsten thin films thus exhibit three different polymorphic variants: α , β , and γ . In all cases reported so far, only two variants were observed to grow simultaneously for the same film; usually, the α - and β -W variants coexist or the α - and γ -W variants form together.

In the present experiments the films consisted of the coexisting α and β variants. To investigate the parameters controlling these variants, a brief description of the experimental conditions is first needed. The tungsten thin films (with a thickness gradient varying from 10.5 to 72 Å) were prepared by thermal evaporation onto VC and ACP NaCl substrates heated at different temperatures. The pressure prior to evaporation was in the low 10^{-9} Torr range which dropped to $5 - 8 \times 10^{-8}$ Torr at the beginning of the evaporation process and finally stabilized in the low 10^{-8} Torr region. The evaporation rate was about 0.035 Å. In all cases, the α -W variant first appears at an average film thickness of 21.1 Å. Then a very weak trace of the β -W variant appears at an average film thickness of 42 Å. The β -W variant finally reaches a peak at 58 Å (as observed by the diffraction patterns), which is the thickness at which coalescence begins. By the end of the coalescence stage, the β variant is partially obscured and by the time the average film thickness reaches 100 Å, the β variant becomes completely obscured. In the growth modes section, we saw that for the α -W variant, the

noncrystallographic particles overwhelm the star-like particles and cause the α PCT's to become obscured. Similarly, the noncrystallographic α particles overwhelm the β particles and cause the β -W variant to become obscured. In one case, however, the coexistent α and β variants were observed to transform sluggishly although completely into the γ phase. This occurred for films obtained on VCS at 350°C at an average film thickness of 72Å, and was observed by electron diffraction.

The effect of the substrate temperature on the β -W variant is now considered. The sequence of wide-area diffraction patterns, Figures 13f (25°C), 12c (150°C), 12f (250°C), and 5f (350°C) show:

- a) that the existence of the β -W variant is temperature independent, since the β -W rings are observed for all substrate temperatures;
- b) that the degree of epitaxial orientation of the β -W variant increases with substrate temperature, since more preferred orientation is observed at 350°C than at 25°C.

The effect of different substrate surface conditions (VCS versus VCPS) is now considered. Since the β -W rings are present in the diffraction patterns of films prepared on both VCS (Figure 13e) and ACPS (Figure 14f), the existence of the β -W variant is thus independent of the nature of the substrate. However, better β -W orientations are obtained on VCS (Figures 5e-f) than on ACPS (Figure 16).

The question arises as to how the β variant is stabilized. The fact that the orientation of the β variant increases with the substrate temperature suggests that β variant is nucleated. However, the nucleation and growth of the β -W variant appears much later than

the nucleation and growth of the α -W variant. This suggests that specific impurities on the substrate surface are needed to stabilize the nucleation of the β -W variant. Support of this view is given by the results of Basavaiah and Pollack.⁽⁵⁸⁾ Their samples prepared at 10^{-6} Torr showed the presence of the β -W variant in all cases. As the pressure decreased, the β -W variant decreased in intensity until at 10^{-9} Torr only α -W remained. The β variant was not found at 3×10^{-9} Torr, probably because their high evaporation rate ($.3\text{\AA}/\text{sec}$ as compared with $0.035\text{\AA}/\text{sec}$ in this work) and the small contamination rate at this pressure did not allow the β variant to nucleate. By increasing the pressure, the contamination rate of the substrate surface is increased, thus favoring nucleation of the β -W. Thus the β -W is favored by a low evaporation rate ($\sim 0.01\text{\AA}/\text{sec}$) and pressure ($\sim 10^{-9}$ Torr) or a high evaporation rate ($\sim 0.5\text{\AA}/\text{sec}$) and pressure ($\sim 10^{-6}$ Torr). Not much work has been done to determine which impurities stabilize the nucleation of the β variant. Basavaiah and Pollack⁽⁵⁸⁾ and Kammerer and Strongin⁽⁵⁹⁾ suggest that oxygen atoms stabilize the β structure. The present research does not refute or confirm this suggestion, and more quantitative work is needed to determine which impurity(ies) stabilizes the β .

A third variant, γ -W, was also observed in this research. Tungsten thin films, having both α - and β -W variants, transformed sluggishly to the γ -W variant. This transformation only occurred for films evaporated on VCS at 350°C . The γ -W phase is thus not nucleated, contradicting the results of Chopra et al.⁽³⁸⁾ The works of Chopra et al.,^(36,37) Miska and Gillet,⁽⁴⁶⁾ and Sella and Coppens⁽⁴⁷⁾ show that the β phase is stable at low temperature, then

transforms to the γ phase around 400°C and then always back to the β phase again at about 700°C . The temperature at which the α to γ transformation occurs varies widely depending upon the substrate and the evaporation technique used. But the parameters that stabilize the γ phase are presently not known.

C. Orientations and Morphologies of Tungsten Thin Films

Several preferential orientations are believed to nucleate at the beginning of the evaporation process. The main one, the (100) orientation, is dominant throughout the nucleation and growth processes. Not much work was done beyond this stage; however a thick tungsten film ($\sim 100\text{\AA}$) obtained by deposition on an ACPS at 25°C shows traces of this orientation (Figure 18). The (100) nuclei are initially square shaped with their diagonal parallel to the $\langle 100 \rangle$ directions of the NaCl surface. Because the corners have a larger area for capturing atoms from surface diffusion, they grow at a faster rate than the edges and the squares transform to an asteroid shape. As the evaporation time increases, the asteroids quickly form star-like shapes with four arms (Figure 4d).

The second PCT found for the α -W variant was also of the (100) type, but rotated 45° relative to the first, with orientation relationship: $\{100\} \langle 100 \rangle \text{W} // \{100\} \langle 100 \rangle \text{NaCl}$. This PCT was found in lesser amounts than the main texture. Since the main and secondary orientations consist of (100) nuclei, the observed shape of the particles is star-like. However, the average diameter of particles having the secondary orientation is much smaller than those having the main orientation ($\langle 110 \rangle \text{W} // \langle 100 \rangle \text{NaCl}$). This size effect is shown in the dark field images of Figures 15c (taken with a (110)

spot) and 15d (taken on the (110) ring, but 45° from (110) spots).

The star-like particles (A) of Figure 15c belong to the main orientation and are larger than the star-like particles (d) of Figure 15d which belong to the secondary orientation. The former presumably have a lower interfacial energy, which favors the growth of the star-like particles with the main orientation over those with the secondary orientation.

Two more PCTs were found in α -W thin films. These textures are $\{110\} \langle 100 \rangle \parallel \{100\} \langle 100 \rangle \text{ NaCl}$ and $\{123\} \parallel \{100\} \text{ NaCl}$ which are about equal in amount but much less than the (100) textures.

Unfortunately, both textures were weak, and dark field microscopy could not be performed to determine the shapes of the particles giving these orientations.

Concerning the particle shapes of the α -W variant, other crystallographic shapes, such as X-shaped and triangular shaped particles, were observed besides the star-like shape. An attempt to find the orientation of the X-shaped particles was unsuccessful either because of their small number or peculiar orientation. Note that the dendritic growth starts much earlier on the X-shaped particles than on the star-like particles (Figure 4d). This may be explained again in term of interfacial interaction.

Table I is a résumé of the work on bcc metals evaporated onto NaCl substrates. Iron, vanadium, chromium, niobium, and tungsten all have the same orientation relationship with the substrate: $\{100\} \langle 110 \rangle \parallel \{100\} \langle 100 \rangle \text{ NaCl}$. The above orientation relationship thus appears representative of bcc metals deposited on NaCl. The evaporated tungsten films obtained in the present work also follow this pattern.

~~However~~, it is important to point out that this (representative) ~~orientation~~ for bcc metals is not unique, although predominant. For ~~example~~, chromium (44) evaporated on AC NaCl exhibits (110) and (120) ~~orientations~~, besides (100) orientations; niobium (35) forms with ~~orientations~~ (110) or (111) orientations, depending upon deposition parameters.

The sequence of electron micrographs, Figures 6a-d, show ~~different~~ morphologies for similar films deposited on VC NaCl at ~~different~~. The deposition parameters (substrate temperature, pressure, ~~evaporation~~ rate, etc.) were meticulously controlled from experiment ~~to experiment~~. So it is unlikely that variations in the deposition ~~parameters~~ could cause these different film morphologies. However, ~~different~~ different morphologies and densities were obtained with the ~~same~~ specimen it is probable that the variable at play is the surface ~~condition~~, i.e, uneven cleavage.

V. CONCLUSIONS

The growth mode of tungsten films grown on vacuum-cleaved NaCl substrates at 350°C is of the Volmer-Weber type. The films exhibit a polycrystalline texture in the early stages of nucleation, growth, and coalescence which disappears as the thickness of the film increases. For lower substrate temperatures, the growth mode initially is of the Stranski-Krastanov type which then changes sluggishly to the Volmer-Weber mechanism as the thickness and temperature of the film increase. The polycrystalline texture formed is more or less perfect, depending upon the substrate temperature. At room temperature, a very weak texture is obtained whereas at 250°C, the texture is similar to that obtained at 350°C.

Several orientations were observed during the nucleation, growth and coalescence of the tungsten film. Except for the main {100} orientation, the others could not be indexed satisfactorily. They are listed below, in decreasing order of comparative frequency:

- a) {100} <110> α -W // {100} <100> NaCl
- b) {100} <100> α -W // {100} <100> NaCl
- c) {110} <001> α -W // {100} <100> NaCl
- d) {123} α -W // {100} NaCl

For tungsten films grown on air-cleaved preheated NaCl substrates, the growth mechanism is of the Volmer-Weber type at 350°C. At room temperature, the initial modes are the Volmer-Weber and the Stranski-Krastanov types which then change to the Volmer-Weber mode as the thickness of the film increases. The difference in growth modes between air- and vacuum-cleaved substrates at room temperature is explained in terms of the interfacial energy. The

films are polycrystalline at low and high temperatures and tend to form a very weak (100) texture at high temperature (350°C).

For the deposition parameters used, a second phase, the A-15 phase, was observed in all films prepared on either vacuum- or air-cleaved, preheated substrates. The β -W phase always displayed the same polycrystalline texture as the β -W phase, except that it was observed later in the growth stage. The main orientations of the β -W structure are given below in decreasing order of importance:

- a) $\{001\} \langle 110 \rangle \beta\text{-W} // \{001\} \langle 100 \rangle \text{NaCl}$
- b) $\{011\} \langle 100 \rangle \beta\text{-W} // \{001\} \langle 100 \rangle \text{NaCl}$
- c) $\{001\} \langle 100 \rangle \beta\text{-W} // \{001\} \langle 100 \rangle \text{NaCl}$

Concerning the shapes of the bcc particles, the formation of star-like particles by dendritic growth is of particular interest. The star-like particles are responsible for the $\{100\}$ preferred orientation. Other particle shapes, such as the X-shape and particles having a three-fold shape could not be explained because their low density did not permit dark field microscopy. For the β -W phase, the particles were clearly crystalline although without definite shapes. However, some have a square or rectangular shape, leading to the $\{100\}$ orientation; others exhibited a rounded rhomboid shape, leading to the $\{110\}$ orientation.

A brief enumeration of other conclusions is given below:

- a) the textures of both the α - and β -W phases are dependent on both the nature (VC versus ACP) and the temperature of the substrate surface;
- b) the formation of the β -phase is temperature independent;
- c) the nucleation of the β -W phase is stabilized by impurities;

- d) the β -structure appears to be independent of the nature (VC versus ACP) of the substrate;
- e) on vacuum-cleaved substrates at 350°C , both the α - and β -W phases transform to a γ -W phase at a thickness of about $72\text{\AA}$. This is contradictory to the results of Chopra et al. (37) which suggest that the γ phase was substrate nucleated.
- f) a combination of low evaporation rates and low pressures seems to favor the β -W structure.

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TABLE I

Comparison of Growth Characteristics and Polymorphic Forms Exhibited by BCC Metals

BCC METALS	MELTING TEMPERATURE (°C)	LATTICE PARAMETER (Å)	HEAT OF SUBLIMATION (kcal/mole)	SURFACE ENERGY (kcal/mole)	POLYMORPHIC VARIANTS	ORIENTATIONS WITH SUBSTRATE	REFERENCES
IRON (Fe)	1535	2.8664	99		bcc fcc	main: {100} <011> Fe // {100} <001> NaCl second: {100} <001> Fe // {100} <001> NaCl not given	(60), (61), (62) (31)
VANADIUM	1710	3.0282	119		bcc fcc	main: {100} <011> V // {100} <001> NaCl others: not given not given	(63) (29)
CHROMIUM	1890	2.8850	80		bcc fcc A-15	main: {001} <110> Cr // {100} <001> NaCl second: {001} <100> Cr // {100} <001> NaCl not given same as the bcc variant	(62), (63), (64) (32) (33), (34), (65)
NIOBIUM	2500	3.3077	172	49	bcc fcc	main: <011> {100} Nb // <001> {100} NaCl others: <001> {100} Nb // <001> {100} NaCl <100> {111} Nb // <001> {100} NaCl main: {001} Nb // {100} NaCl	(35) (35), (66)
MOLYBDENUM	2620	3.1468	157	43	bcc fcc	polycrystalline film polycrystalline film epitaxial on NaCl	(28) (28) (38)
TANTALUM	2996	3.3058	187		bcc fcc β -Ta	T > 300°C, {001} Ta // {100} MgO T > 300°C, {001} Ta // {100} MgO <011> {100} Ta // <011> {100} NaCl epitaxial on in situ cleaved MgO	(28) (28) (38) (67)
TUNGSTEN	3370	3.1652	203	53	bcc fcc A-15	main: <110> {001} W // <100> {001} NaCl epitaxial on LiF main: <100> {001} W // <001> {100} NaCl epitaxial on LiF not given	(47) (46) (37), (38), (47) (46) (36), (58)

TABLE II

The s-Values of Maxima of the Evaporated Carbon Films and Some (hkl) Reflections of Tungsten

Evaporated carbon film		Tungsten crystal	
no. of maximum	s-value ($\text{\AA}^{-1}$)	(hkl)	s-value ($\text{\AA}^{-1}$)
1	1.2		
2	2.9	(110)	2.80
		(200)	3.97
		(211)	4.87
3	5.5	(220)	5.60
		(310)	6.28
		(222)	6.89
		(321)	7.44
		(400)	7.95
4	8.6	(330), (411)	8.44
		(420)	8.89

TABLE III

Sublimation Rates of Cleaved Sodium Chloride

Temperature	Rate of mass loss	Monolayer sublimation 1 hr (assuming a roughness factor of unity)
322	0.0053	.00334
357	0.0772	.04846
408	1.46	.92
412	1.77	1.12
435	5.56	3.5
440	7.07	4.45
450	13.3	8.38
459	19.9	12.54

TABLE IV

Calculated Spacing of the hkl Rings of Both α - and β -W Structures

A-15 ($a=5.036\text{\AA}$)			bcc ($a=3.165\text{\AA}$)		
$N^2 =$ ($h^2 + k^2 + l^2$)	(hkl)	C/d_{hkl}	C/d_{hkl}	(hkl)	$N^2 =$ ($h^2 + k^2 + l^2$)
4	200	1.882			
5	210	2.105	2.121	110	2
6	211	2.306			
12	222	3.260	3.000	200	4
13	320	3.394			
14	321	3.522			
16	400	3.765	3.674	211	6
20	420	4.209	4.242	220	8
21	421	4.313			
22	332	4.415			
29	520	5.068	4.743	310	10
30	521	5.155	5.196	222	12
32	440	5.324			
36	600	5.647	5.612	321	14
37	610	5.725			
38	611	5.802	6.000	400	16

Figure 1. The basic growth modes: a, the Volmer-Weber mode, b, the Frank-van der Merwe mode, and c, the Stranski-Krastanov mode.

Figure 2. Apparatus used for preparation of thin films: a, the filament holder; b, substrate cleaver-shutter; and c, substrate holder-heater.

Figure 3. Substrate holder used for the preparation of thin films. Figure 3a is a side view showing how the NaCl rods are cleaved. Figure 3b is a top view showing the drilled holes arranged in seven rows, in which the NaCl rods are inserted.

a

b

Figure 4. Growth sequence for films deposited on substrates at 350°C which were vacuum-cleaved just prior to deposition.

	<u>Magnification</u>	<u>Average thickness</u>
a	X200,000	10.5Å
b	X200,000	21.0Å
c	X500,000	31.5Å
d	X200,000	42.0Å
e	X200,000	52.5Å
f	X200,000	63.0Å
g	X200,000	73.5Å

b **c**

d

e

d

e

f

g

Figure 5. Wide-area diffraction patterns corresponding to Figure 4.
Average film thicknesses are:

a 10.5Å
b 21.0Å
c 31.5Å
d 42.0Å

e 52.5Å
f 63.0Å
g 73.5Å

a

b

c

d

f

e

Figure 6. a, b, c, and d are a sequence of micrographs showing different particle densities and morphologies found for similar films deposited on substrates at 350°C which were vacuum-cleaved just prior to deposition. The average film thickness is 31.5Å. X200,000

a

b

C

D

Figure 7. Three main polycrystalline textures encountered on tungsten thin films evaporated on vacuum-cleaved NaCl. a, $(100) [110] \text{ W} // (100) [100] \text{ NaCl}$, b, $(100) [100] \text{ W} // (100) [100] \text{ NaCl}$, and c, $(110) [001] \text{ W} // (100) [100] \text{ NaCl}$.

Figure 8. a, bright field; b, dark field; and c, wide-area diffraction pattern of W-films deposited on substrates at 350°C which were vacuum-cleaved just prior to deposition. The average film thickness is 47.5Å. X200,000.

b

Figure 9. High resolution diffraction pattern of a tungsten thin film evaporated on vacuum-cleaved NaCl at 350°C. The average film thickness is about 52Å. Diffraction rings from both the α - and β -W structures are clearly displayed.

Figure 10. High resolution diffraction pattern showing α - and β -W lines. This electron micrograph is the same as in Figure 9.

 α -W

 β -W

Figure 11. Growth sequence for films deposited on substrates at 150°C and 250°C which were vacuum-cleaved just prior to deposition. X200,000.

<u>Average film thickness</u>	<u>150°C</u>	<u>250°C</u>
31.5Å	a	d
52.5Å	b	e
72.5Å	c	f

a

d

b

e

c

f

Figure 12. Wide-area diffraction patterns corresponding to Figure 11.

<u>Average film thickness</u>	<u>150°C</u>	<u>250°C</u>
31.5Å	a	d
52.5Å	b	e
72.5Å	c	f

a

d

b

e

c

f

Figure 13. Growth sequence for films deposited on substrates at room temperature which were vacuum-cleaved just prior to deposition. X200,000.

<u>Average film thickness</u>	<u>Bright field image</u>	<u>diffraction pattern</u>
31.5Å	a	d
52.5Å	b	e
72.5Å	c	f

a

d

b

e

c

f

Figure 14. Growth sequence for films deposited on substrates at 450°C which were vacuum-cleaved just prior to deposition. X200,000.

<u>Average film thickness</u>	<u>Bright field image</u>	<u>diffraction pattern</u>
63Å	a	c
84Å	b	d

a

b

Figure 15. Tungsten thin film evaporated on vacuum-cleaved KCl substrate at 350°C: a, bright field image; b, wide-area diffraction pattern corresponding to the region in a; c, dark field micrograph taken with a (110) spot of the α -W phase and d, dark field image taken with a (200) spot of the β -W phase.

b

Figure 16. Growth sequence for films deposited on air-cleaved, preheated substrates. The temperature of the substrates was 350°C during deposition.

<u>Average film thickness</u>	<u>Mag.</u>	<u>Bright field image</u>	<u>diffraction pattern</u>
21.0Å	X50,000	a	d
31.5Å	X200,000	b	e
52.5Å	X200,000	c	f

2

a

d

b

e

c

f

Figure 17. Growth sequence for films deposited on air-cleaved, preheated substrates. The temperature of the substrates was 25°C during deposition. X200,000.

<u>Average film thickness</u>	<u>Bright field image</u>	<u>Corresponding diffraction pattern</u>
21.0Å	a	d
31.5Å	b	e
42.0Å	c	f

a

d

b

e

c

f

Figure 18. High resolution diffraction patterns of tungsten thin films deposited on air-cleaved, preheated NaCl substrates. The temperature of the substrates was 25°C during deposition.

<u>Average film thickness</u>	<u>HRDP</u>
100Å	a
150Å	b

a

b