Annual Technical Progress Report V

"In-Situ" Electron Microscope Investigation of the Nucleation
and Growth of Sputtered Thin Films

by

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I. Introduction.

Work during the past year has been concentrated in three areas. First, the continuous in situ study of the nucleation and growth of sputtered thin films inside the electron microscope. Further results of experiments on the growth of niobium and silicon thin films on substrates of graphite and mica will be given in the later sections of this report. The second area is the in situ deposition of sputtered thin films on single crystal silicon substrates. A method to produce thin silicon substrates suitable for in situ deposition has been developed. Results of nucleation studies of silver and silicon sputter-deposited on single crystal silicon substrates have been obtained. Thirdly, the ultra-high vacuum stage is in final assembly. A high-speed diffusion pump-high conductance liquid nitrogen trap system has been designed to replace the turbo-molecular pump. An improved Granville-Phillips electro ion pump was obtained in exchange for the earlier model.

II. Niobium Deposition on Graphite and Mica.

Studies of niobium deposition on single crystal graphite were performed by the in situ electron microscope ion beam sputtering technique. The instrumentation was discussed in detail in the published paper (1). The graphite substrates were produced by the mechanical method described in the previous progress report (1972).

It was reported last year that the growth of niobium on single crystal graphite occurs either by nucleationless formation possibly by monolayer growth or by nucleation at a size smaller at coalescence than the resolution limit of the microscope. Further experiments performed at higher substrate temperatures clear this uncertainty. The nucleation and liquid-like coalescence of niobium thin films were observed at substrate temperatures as low as 780°C, however, the coalescence stage of the niobium islands occurred at a size of roughly 10 angstroms. Experiments performed at 1040°C at a deposition rate of 5 Å/min shows that the saturation density of islands is of the order of $4 \times 10^{12} \text{ cm}^{-2}$ and liquid-like coalescence occurs at nucleus size of about 20 angstroms. Figure 1 shows time sequenced micrographs of niobium deposited on graphite at this temperature. It is worthwhile to note that at 1040°C substrate temperature after the channel stage, a fascinating structure which looks like fish scales with a mean diameter of about 200 angstroms forms, while at 780° substrate temperature, a different feature appears which is shown in Figure 2.

Large differences exist in the microstructure of the high temperature films (>780°C) and those deposited at temperature less than 650°C. Both the direct electron image and the electron diffraction patterns exhibit altered structure. In particular, the low index rings of diffraction pattern from the low temperature deposits show a six-fold symmetry in the "texture" pattern (Figure 3a) while the high temperature pattern shows twelve fold symmetry of the same rings (Figure 3b). The effect is most certainly

due to increased double positioning of the niobium nucleus at higher temperature as well as much accentuated twinning of the nuclei.

In addition, a rather marked change in lattice constant of the niobium occurs. Films grown at 480°C have a lattice constant of 4.45 angstroms while between 650°C and 870°C the lattice constant is 4.51 angstroms and at 1080°C it becomes 4.58 angstroms. In all cases the films grow in the face-centered cubic crystal structure as reported for Nb on MgO by Hutchinson (2) but show no thickness dependence on structure.

Niobium has been sputter-deposited on mica at a substrate temperature of 410°C . The size of nuclei formed was clearly less than the microscope resolution however the diffraction pattern (Figure 4a) shows the now expected face-centered cubic structure. At later stages of growth the crystalline contrast due to elements of perhaps $50\text{\AA}$ in size, become evident (Figure 4b). These are due to grain growth of the original nuclei. The nucleation kinetics are out of reach of this experiment due to the very early point at which complete coalescence occurs.

III. Silicon Deposition on Graphite.

In situ sputter deposition of silicon on graphite substrates has been performed inside the electron microscope. The graphite substrates were prepared by the same procedure used for the niobium deposits on graphite. The results of these silicon on graphite experiments are

somewhat unexpected. When the deposition starts, before the formation of any silicon nuclei, a thin layer of β -SiC film forms on the graphite substrate. The silicon islands were observed to occur on β -SiC after the β -SiC grew to a complete film, generally after 1800 seconds deposition, which yields a mean thickness of roughly 150 angstroms. The mechanism of growth then is similar to the "interaction epitaxy" mechanism proposed by Hutchinson (2).

Figure 5 shows the formation of β -SiC films at a substrate temperature of 865°C . Liquid-like coalescence occurs at a mean thickness of roughly 50 angstroms. The dependence of observed β -SiC islands density on deposition is shown in Figure 6. Figure 7 is a typical diffraction pattern of such a film on a single crystal graphite substrate deposited at a temperature higher than 800°C . It shows a ZnS crystal structure with a lattice constant of 4.38 angstroms.

The growth of silicon on β -SiC film at this temperature (865°C) is shown in a cine film accompanying the report and labeled Figure 8 which was taken by a 16 mm motion picture camera mounted under the microscope column and photographing a phosphor image screen. It should be noted that the density of silicon islands increases with deposition time. While some silicon islands grow, new islands continue to appear on the SiC film. No liquid-like coalescence phenomenon was observed in this case, instead, a "budding" phenomenon leading to a layered configuration of the silicon islands occurs. The buds grow and produce more buds. This phenomenon is shown in Figure 9.

A reasonable explanation for such a phenomenon may involve a slight contaminant layer which may increase in mean thickness with time and form a barrier to both further total growth and coalescence. Local areas on the nucleus may then form preferred sites for the "budding" growth observed.

The diffraction pattern of this Si-SiC-graphite film shown in Figure 10 indicates the occurrence of two different structures. The diffuse rings are caused by the fine-grained β -SiC film, while the spotted rings are due to silicon crystalline of larger grain size. The index of this diffraction pattern with regard to crystal plane is given in Table 1. The lattice constant determined for silicon is 5.42 angstroms while that for β -SiC is 4.36 angstroms.

One experiment was performed at a lower substrate temperature of 730°C. The diffraction pattern and micrograph before and after the formation of silicon islands are shown in Figure 11. The average diameter of the silicon islands is roughly 100Å. A higher substrate temperature (960°C) produced a β -SiC film on which no silicon islands were observed. Figure 12 shows that the β -SiC film was not in the channel stage even after 2 hours deposition. Clearly all the silicon was either interacted with carbon to form SiC or was evaporated from the surface. There is much evidence that considerable reevaporation did occur since the mean film thickness at any point in the deposition was always a fraction of that observed at lower temperatures.

IV. Preparation of Single Crystal Silicon Substrates for In Situ Deposition.

A single crystal silicon substrate suitable for in situ deposition should at minimum fit the following three conditions. First, it should be very thin, otherwise the small nuclei of the deposit can not be observed and the diffraction pattern of the deposited "thin" film may also be overwhelmed by that of the thick substrate. Secondly, it should be microscopically flat, any surface irregularity may be confused with deposited nuclei. Complications in the nucleation and growth mechanism may also occur such as preferential nucleation. Thirdly, the substrate should be "clean". Although in the present condition, no in situ substrate cleaning apparatus is available, extreme care must be taken during the substrate preparation procedure.

There are two general methods for the preparation of thin silicon specimens for transmission electron microscopic examination. Jet chemical polishing is a quick method, however thin, flat surface suitable for in situ studies can not generally be obtained. Ion beam thinning can produce suitable thin silicon, but it is a time consuming process. Contaminants have also been observed on the silicon after ion beam bombardment. They may be caused either by the interaction of the ion beam with hydrocarbons present in the vacuum system, or by some contaminant material sputtered on the substrate by the stray ion beam.

The method developed for the present study is a combination of the jet chemical etching and a modified ion beam thinning technique.

Thin, flat, and clean silicon can be obtained by this method without lengthy ion beam thinning.

The apparatus used for jet chemical polishing is shown in Figure 13a, the polishing solution contains 9 parts HNO_3 (70%) and 1 part of HF (50%). Figure 13b shows the dimension of the silicon substrate before and after jet polishing. A specimen of thickness roughly 0.010 inch is used due to the brittle nature of silicon.

After initial jet chemical polishing, the silicon specimen is transferred to the "Commonwealth" ion thinner and bombarded from both sides with a 7 kilovolt argon ion beam at a current of about 100 microamperes. The bombarding angle is between 20 and 25 degrees. A pin hole occurs in the center of the specimen after about two hours of ion bombardment. After the pin hole is observed, the specimen is transferred again to a silicon-base holder as shown in Figure 14. The use of a silicon base holder was found necessary as a result of contaminant influence on the substrate which causes preferred sites for nucleation. The contaminants were traced to the stainless steel holder of the ion thinner and the gravity holder system for single side bombardment was devised. After ten minutes of ion beam bombardment of the first face, the silicon specimen is inverted to allow the bombardment of the second face which is used in the in situ deposition. Since the diameter of the ion beam is larger than the silicon specimen, the entire surface of the specimen on the silicon-base holder is immersed in the ion beam, any contaminants

remaining on the surface are removed. The silicon base below the specimen is made of 1600 ohm-cm, p type single crystal silicon, same as the specimen. Ion beam penetrated through the pin hole may sputter silicon from the base and deposit it on the bottom face of the specimen, but little contaminant is expected on the top surface.

Figure 15a is a diffraction pattern of one thin area around the pin hole of the specimen. The amorphous rings are due to the formation of a thin amorphous silicon surface layer caused by ion beam bombardment. After annealing in the microscope hot stage at temperatures above 600°C, the amorphous rings disappear as shown in Figure 15b.

V. Silver Deposition on Single Crystal Silicon.

Consistent results have been obtained for the in situ deposition of silver on the (111) plane of thin single crystal silicon. The general features of the process of nucleation and growth are qualitatively the same as the deposition of silver on mica and graphite. A sequence of micrographs shown in Figure 16 were taken during sputter-deposition at a substrate temperature of 605°C and a deposition rate in the order of 50Å/min. Generally, nucleation takes place at apparently random sites on the substrates, nuclei increase in size and number, eventually coalesce to form fewer but larger islands which link to form the final film.

Determinations of the number density of islands as a function of time yields a family of curves as shown in Figure 17a and Figure 18a. These curves show variations in initial slope and maximum island density with both temperature and rate of deposition. The curve of $\log N_S$ (N_S is the saturation islands density) vs $1/T$ is plotted in Figure 17b. By the application of the Stowell-Hutchinson theory (3), a value of 0.51 eV (sum of the adsorption, binding, and diffusion energy) is found from the slope of this straight line. The value of the pre-exponential term is found to be 8.9×10^9 nuclei/cm² from the interception on the ordinate by letting $1/T$ equal to zero. Figure 18b shows the dependence of saturation islands density on the deposition rate. These data indicate a dependence on incident rate J of a value between one and two in the exponent (i.e., between linear and square). This value is at odds with theory and will be discussed in a latter section.

The silver films deposited at substrate temperature of 605°C grew with a perfect (111) orientation parallel to the silicon substrate. At lower substrate temperature, polycrystalline islands occurred. Figure 19 shows micrographs of a silver film with an average thickness in the range of 500 angstroms. The film shown in Figure 19a was deposited at 605°C substrate temperature, while that of Figure 19b was at 518°C. The variation in contrast on the single islands of (b) reveal that they grow with random orientation.

Figure 20a is the diffraction pattern of a film deposited at a substrate temperature 605°C . The index of the pattern is given in Figure 21. The weak $1/3(4\bar{2}2)$ spot may be caused by the double diffraction from the twinned single crystal films as suggested by Pashley and Stowell in the case of gold film (4). The diffraction pattern of a film deposited at 518°C substrate temperature is given in Figure 20b. The rings are composed of spots, which is a result of the diffraction from randomly oriented grains in the silver islands. Silver deposited at 420°C has a grain size finer than the film deposited at 518°C . The diffraction pattern is shown in Figure 20c. The film grows with a preferred (111) orientation parallel to the substrate. No double reflection spots occur in this case.

VI. Silicon Deposition on Silicon

Silicon has been in situ sputter-deposited on the (111) plane of single crystal silicon substrates. The sputtered silicon atoms bond together and form discrete three-dimensional islands. These islands can be observed in the electron microscope if the substrate temperature during deposition is higher than 570°C . At lower temperature the silicon islands coalesce at a size near the limit of resolution of the microscope which makes the direct observation difficult.

A sequence of micrographs showing the nucleation and growth of the silicon islands at 700°C substrate temperature is presented in Figure 22. The deposition rate is on the order of $20\text{\AA}/\text{min}$. The islands

generally are observed after 300 seconds deposition, and increase both in number and in size with time until liquid-like coalescence becomes prominent. The small variation in contrast between the silicon islands and the substrate, as well as the irregular shape of the periphery of the islands indicates that these islands are thin in the substrate normal direction. The contrast of each single island is virtually identical, which suggests perfectly aligned epitaxial growth of these films.

The occurrence of liquid-like coalescence depends markedly on substrate temperature. At lower temperatures, coalescence occurs at an earlier time with a smaller island size. Two micrographs from an experiment performed at the same deposition rate as the previous sequence (700°C), but with 570°C substrate temperature are shown in Figure 23.

The dependence of islands density on deposition time of these two experiments is illustrated in Figure 24. The number density of nuclei varies by a factor of three between these two cases.

Figures 25 and 26 show two sequences of diffraction patterns of the above experiments. Both show single crystal growth of the silicon films and the perfect parallel orientation with respect to the substrate surface. The satellites spots appeared on Figure 25c characterize the features of stacking faults and twins of a thick film. The strong $1/3(4\bar{2}\bar{2})$ diffraction appeared in Figure 26c is not completely understood as yet.

VII. Ultra High Vacuum In Situ Deposition System.

Efforts have been made during the past year to improve the vacuum of the ultra high vacuum system, which include baking the system, changing the transmission of the turbo-molecular pump, and reducing the outlet pressure of the turbo-molecular pump. No satisfactory improvements have been obtained. Methods have also been investigated to eliminate the vibration on the ultra high vacuum chamber transmitted from the turbo-molecular pump. No simple and secure method has been found. It was then concluded that the best and most economical way to solve these problems was to replace the turbo-molecular pump by a high speed diffusion pump-high conductance liquid nitrogen trap system.

A NRC VHS-6 diffusion pump and a Granville-Phillips low profile trap have already been purchased. The Granville-Phillips series 217 Ion Pump has been modified to series 220 mod 02 configuration. No further problems are expected to occur prior to mounting and testing of the ultra-high vacuum on the electron microscope.

The construction of the quadropole mass spectrometer is complete. Preliminary testing inside an ultra high vacuum chamber has shown satisfactory performance.

VIII. Discussion of Results.

Experimental results in the area of in situ observation of the nucleation and growth process of thin films of several interesting substrate overgrowth combinations have been obtained in recent months. Some of these have been the subject of analysis and the findings have been published in the Journal of Vacuum Science and Technology (Jan. 1973) and Reviews of Scientific Instruments (Dec. 1972). Other results have not been subject to rigorous analysis and will be presented in preliminary form in this report.

The real substance of a nucleation and growth experimental result lies in its bearing on the mechanism of initial nucleation and subsequent crystal growth to form a thin film. The results reported here form a substantial base of new data for the in situ ion beam deposition system and indeed for several entirely unexplored overgrowth-substrate combinations hitherto beyond the reach of experiment.

VIIIa. Niobium on Graphite and Mica.

The face-centered cubic modification of niobium (first reported by Hutchinson (2) and later confirmed in numerous other normally body-centered cubic metals by others) has been observed and studied more closely in the two systems investigated. In both cases the face-centered cubic structure was evident even in the earliest stage of growth

(<10 angstroms mean thickness) as noted by careful transmission electron diffraction.

The systems differ however in that niobium sputtered on graphite form nuclei of observable size ($10\text{\AA}$) at 790°C while deposits on mica show evidence of crystalline material at low temperature (500°C) but no observable nuclei since the temperature cannot be raised above 500°C due to degradation. It is likely that the size of nucleus is reduced at the coalescence stage by the two coupled effects of lower diffusion distance on the substrate and higher evaporation energy. Both of these may be attributed to a high defect density on the surface however no theory of sufficient generality exists to allow analysis of such systems without resort to computer calculations. The theory of Stowell and Hutchinson will be applied to the system in order to extract the surface defect approximations.

The mechanism of growth of the niobium on graphite at temperatures greater than roughly 1000°C is one of growth to a diameter of about $200\text{\AA}$ followed by formation of one or more points of 'renucleation'. Presumably a film of contaminant forms over the nucleus during growth which increases in thickness and finally inhibits growth. New areas of high nucleation potency are formed, possibly by stress cracking of the contaminant film, which initiate further growth. The curious "budding" growth also seems responsible for the structures seen in high temperature growth of silicon on graphite. In both cases interaction of the overgrowth with the substrate is likely.

VIIIb. Silicon on Graphite

Direct confirmation of the interaction epitaxy mechanisms first proposed by Hutchinson was found in the formation of β -SiC upon deposition of silicon on graphite. Formation of the β -SiC film by classical nucleation and growth to $150\text{\AA}$ was followed by nucleation of a silicon film again by classical means, however followed by the budding growth previously described.

The quite remarkable growth of β -SiC of Figure 6 is, however, worthy of note. The kinetics of the growth process are reversed from non-interaction cases in that the maximum island density while being reduced with increasing temperature is also seen to occur at an earlier rather than a later time. This clearly indicates an interaction (or reaction) limited growth rather than the classical surface diffusion limited case.

These results along with those described in the previous section are of great practical importance to those involved with the production of thin films and will be reported in detail for this reason. They do however shed little light on questions of nucleation which can be treated theoretically. Consequently, the results of deposits on the much better controlled silicon substrates described in latter sections are of greater value to this immediate study.

VIIIc. Silver on Silicon

The data obtained for silver on silicon although very preliminary are gratifyingly self consistent and reproducible. The curves of island density with time are well behaved and, due to the single crystal nature of the substrate are easy to count to very low values of the density at an early stage of growth. The values of both the pre-exponential term and the energy sum term are well within the limits expected from theory. These data indicate a value of one for the initial nucleus size which is in agreement with most data on similar studies.

The dependence of the incident rate with temperature is not nearly so well behaved. While the N_s (maximum island density) vs J curve is best fit by the first power in J , the square term is nearly as good. Both experiment and theoretical faults can be blamed for this discrepancy. Further experiments are clearly indicated.

The transformation from polycrystal to very perfect single crystal at 500-600°C is of great interest. No experiments in controlled vapor deposition are available for comparison.

VIIIId. Silicon on Silicon

The first direct observation of silicon deposited on silicon in the electron microscope has been made in these studies. This work is also in the early stages. The reproducibility noted in the last section carries

over for these substrates as well. The results are consistent and well behaved.

The nucleation process in this case is by island formation in all cases, although a two dimensional growth process is indicated for perfectly clean silicon as a substrate for ideally pure silicon. The presence of an oxide (etc.) layer over the silicon is a certainty and causes the island growth phase. This layer is most certainly of nearly the same surface energy as silicon, however, since the islands have a nearly zero contact angle and coalesce at a very early stage. Further, the layer is either discontinuous or epitaxed since epitaxial growth of the silicon deposit occurs over a very wide range of temperature.

The two curves of Figure 22 are of a most revealing shape. The lower temperature curve shows a negative curvature in the early stage prior to N_s . This indicates a secondary nucleation process in action. The number of nuclei coming into view is greater than linear with time up to N_s . This would indicate an increase in the net number of site nucleated and "available." These sites are most certainly impurity film irregularities, which are likely time and temperature dependent and must be treated by an applicable theory. The Stowell-Hutchinson theory will be applied.

IX. Conclusions.

The work reported in this progress report is an introduction into "hard" data of a quantitative nature from the "in situ" electron microscope technique. The key to this attainment is the development of the technique of consistent production of thin, clean, silicon single crystal substrates. The natural properties of and wealth of data on silicon surfaces enhances the value of this material as a substrate. Superbly reproducible depositions of silver and silicon have been obtained by this technique. The sole remaining step to characterization of a large number of materials (including compounds) in the nucleation and growth process on the highly important silicon substrates, is attainment of ultrahigh vacuum in the substrate area. This is in progress. Prior to its completion much further data of both a fundamental and practical nature can be obtained.

References

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3. M. J. Stowell and T. E. Hutchinson, Thin Solid Films 8, 41 (1971).
4. D. W. Pashley and M. J. Stowell, Phil. Mag. 8, 1605 (1963).

Table 1. Data from diffraction pattern obtained from silicon on graphite experiment.

Ring	Ring Diameter D (cm)	h k l	$D^2/(h^2 + k^2 + l^2)$
1	1.52	Si (111)	.770
2	1.88	β -SiC(111)	1.18
3	2.47	Si (220)	.763
4	2.88	Si (311)	.754
5	3.07	β -SiC(220)	1.18
6	3.49	Si (400)	(.761) weak
7	3.59	β -SiC(311)	1.17
8	3.78	Si (331)	.752
9	4.24	Si (422)	.749

Figure Captions

1. Growth sequence of niobium on graphite. $T = 1040^{\circ}\text{C}$.
2. Niobium on graphite (average thickness about $200\text{\AA}$). $T = 780^{\circ}\text{C}$.
3. Electron diffraction patterns.
 - (a) Niobium on graphite. $T = 650^{\circ}\text{C}$.
 - (b) Niobium on graphite. $T = 1080^{\circ}\text{C}$.
4. Niobium on muscovite mica. $T = 410^{\circ}\text{C}$.
 - (a) Electron diffraction pattern.
 - (b) Micrograph of $250\text{\AA}$ thick film.
5. Growth sequence of β -SiC on graphite. $T = 865^{\circ}\text{C}$.
6. Island number density vs. time for β -SiC on graphite.
7. Electron diffraction pattern of β -SiC.
8. Growth sequence of silicon on β -SiC.
9. Budding growth phenomenon of silicon on β -SiC.
10. Electron diffraction pattern of Si-SiC-graphite film.
11. Micrographs and diffraction patterns of silicon deposited on graphite before and after the formation of silicon islands. $T = 730^{\circ}\text{C}$.
12. β -SiC film on graphite. $T = 960^{\circ}\text{C}$.
13.
 - (a) Jet chemical polishing apparatus.
 - (b) Silicon before and after jet polishing.
14. Silicon base holder.
15. Electron diffraction patterns of ion beam bombarded Si before and after annealing.
16. Growth sequence of silver on silicon.
17.
 - (a) Island number density vs. time for silver on silicon as a function of temperature.
 - (b) A plot of saturation density (N_s) vs. $1/T$ for silver on silicon.

18. (a) Island number density vs. time for silver on silicon as a function of deposition rate.
(b) Dependence of saturation island density (N_s) on the deposition rate for silver on silicon.
19. Silver on silicon with average film thickness 500 angstroms.
(a) $T = 605^\circ\text{C}$
(b) $T = 518^\circ\text{C}$
20. Electron diffraction patterns of silver on silicon.
(a) $T = 605^\circ\text{C}$
(b) $T = 518^\circ\text{C}$
(c) $T = 420^\circ\text{C}$
21. The index of electron diffraction pattern shown in Figure 20(a).
22. Growth sequence of silicon on silicon. $T = 700^\circ\text{C}$.
23. Silicon on silicon. $T = 570^\circ\text{C}$.
24. Island number density vs. time for silicon on silicon.
25. Sequence of electron diffraction pattern at different film thickness.
 $T = 700^\circ\text{C}$.
26. Sequence of electron diffraction pattern at different film thickness.
 $T = 570^\circ\text{C}$.

(a) 26 sec.
160,000X

(b) 79 sec.
160,000X

(c) 150 sec.
160,000X

(d) 431 sec.
160,000X

(e) 739 sec.
160,000X

(f) 2850 sec.
160,000X

Figure 1.

160,000X

Figure 2.

(a)

(b)

Figure 3.

(a)

(b)
160,000X

Figure 4.

(a) 100 sec.
160,000X

(b) 375 sec.
160,000X

(c) 467 sec.
160,000X

(d) 1294 sec.
160,000X

(e) 1701 sec.
160,000X

(f) 2718 sec.
160,000X

Figure 5.

Figure 6.

Figure 7.

Figure 9.

Figure 10.

Before formation
of Silicon Islands

After Formation
of Silicon Islands

(a)
160,000X

(b)

Figure 11.

160,000X

Figure 12.

Jet Chemical Polishing Apparatus

Figure 13(a)

Figure 13(b)

Figure 14.

(a)

(b)

Figure 15.

(a) 32 sec.
160,000X

(b) 84 sec.
160,000X

(c) 125 sec.
160,000X

(d) 163 sec.
160,000X

(e) 463 sec.
160,000X

(f) 600 sec.
160,000X

Figure 16.

Figure 17(a)

Figure 17(b)

Figure 18(a)

Figure 18(b)

(a)
160,000X

(b)
160,000X

Figure 19.

(a) 605°C

(b) 518°C

(c) 420°C

Figure 20.

Silicon $\odot$
Silver $\circ$

Figure 21.

(a) 558 sec.
160,000X

(b) 1402 sec.
160,000X

(c) 3249 sec.
160,000X

Figure 22.

(a) 843 sec.
160,000X

(b) 1251 sec.
160,000X

Figure 23.

Figure 24.

(a) 5 min. (100 Å)

(b) 10 min. (200 Å)

(c) 30 min. (600 Å)

Figure 25.

(a) 0 min.

(b) 15 min. (300 Å)

(c) 45 min. (900 Å)

Figure 26.