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ION POLISHING OF OPTICAL SURFACES

Westinghouse Research Laboratories
Pittsburgh, Pennsylvania 15235

September 1976

Final Report



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AIR FORCE WEAPONS LABORATORY
Air Force Systems Command
Kirtland Air Force Base, NM 87117

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This technical report has been reviewed and is approved for publication.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) In this study, various combinations of ion polishing and vacuum annealing were used in an attempt to reduce the optical absorptance and to smooth the surfaces of polycrystalline metal mirrors for high power lasers. The samples included micromachined copper and conventionally polished copper and molybdenum mirrors. It was found that ion polishing and vacuum annealing resulted in a large decrease 40 to 50%, in the absorptance at 10.6 μ m for conventionally polished copper samples and a small decrease, 5 to 10%, in the absorptance of micromachined copper and conventionally polished molybdenum mirrors. After ion polishing and			

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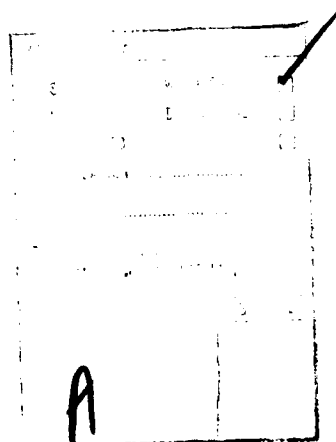
annealing, the absorptance of the conventionally polished copper mirrors was as low as that of the micromachined mirrors. Ion polishing proved beneficial in removing surface defects, such as machining marks, scratches, and embedded polishing grit, and oxide layers; however, for large amounts of material removed, differential sputtering of the various crystallites led to grain boundary delineation and surface roughening. Thus, there exists an optimum amount of material to be removed by ion polishing which results in both maximum removal of surface defects and minimum roughening of the surface. The optimum amounts were found to be: 2500 to 5000 Å for micromachined copper, 5000 to 7000 Å for conventionally polished copper, and less than 1500 Å for molybdenum. Vacuum annealing of copper mirrors at 325°C for 1-1/4 hours yielded a decrease in absorptance after ion polishing but at the expense of grain boundary enhancement; however, vacuum annealing of molybdenum at 800°C for 1 hour resulted in a decrease in absorptance with no evidence of surface roughening. The Knoop microhardness of the conventionally polished copper was initially higher than that of the micromachined copper, but after annealing both at 450°C, the opposite was true. The micromachined sample became progressively softer with annealing at 250°, 325°, 450°, and 600°C, while the conventionally polished sample became softer in one large step, after the 450°C anneal. Finally, it was found that ultrasonic cleaning in various organic solvents caused visible surface damage to copper mirrors, but no such damage was observed on molybdenum samples. The damage to the copper mirrors did not result in an increase in absorption at 10.6 μm.

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PREFACE

The authors wish to thank Capt. J. R. Buckmelter, technical monitor during the major portion of this work, and Capt. R. A. House, who served as monitor during the latter part of this study, for their continued interest and helpful discussions. Thanks are also due to Capt. J. Gowan for the Auger analyses and useful suggestions. The authors thank R. M. Slepian for the hardness measurements and several informative discussions. Finally, the authors acknowledge J. Yurcak and W. F. Toth for operation and maintenance of the ion polisher.



I. INTRODUCTION

Mirrors for high power laser application must of necessity exhibit very low optical absorptivity at the appropriate wavelength. The mirrors must have the proper optical figure, be smooth to minimize light scatter, and have high thermal conductivity to prevent surface damage and undesirable mechanical stresses. To obtain near-theoretical absorptivity, the surface must also be smooth and damage free (ref. 1). Certain metals that have the appropriate properties, such as copper and molybdenum, are candidates for laser mirror substrates. However, conventional polishing of metals usually damages the surface being polished; the depth of the damage depends on the hardness of the material and on the hardness and size of the polishing grit used. In addition, polishing grit may be embedded in or just below the surface. The use of electropolishing or etching frequently can be effective, except that a residue may be left on the surface from the chemical reaction and, moreover, the surface figure is usually distorted. The combination of damage plus residue resulting from the polishing leads to surfaces with higher absorptivity, lower thermal conductivity, and lower damage threshold.

In a previous study, (ref. 2) we demonstrated the efficacy of an alternate approach, ion polishing, for removing material from surfaces in a controlled manner, minimizing the damage to the surface and eliminating contamination. Ion polishing relies on the sputtering of surface atoms by bombarding gas ions; however, it is unlike conventional sputtering in which the surface is bombarded by ions at near normal incidence, leaving the surface damaged and roughened. With the ion polisher used here, a scanned and focused beam of relatively low energy ions is incident on the surface at a glancing angle. This maximizes sputtering yield and should preferentially remove high spots, resulting

in a smoother surface. The ion beam is programmed to move across the sample surface, and the sample is simultaneously rotated in order to avoid surface texturing and to optimize smoothing.

In the aforementioned study in which conventionally polished, single crystal, copper samples were used, a combination of ion polishing and vacuum annealing yielded smoother sample surfaces and a significant decrease in the absorptance, for example from 0.91% to 0.76%, at a wavelength of 10.6 μm . SEM micrographs of the sample surface showed that scratches, as well as polishing grit which became embedded in the surface during the prior conventional polishing, were removed by the ion polishing. The sequence of ion polishing and vacuum annealing was also applied to single crystal copper samples which had been electropolished and yielded similar results, i.e., a decrease in absorptance and the removal of residue left by the electropolishing. The decrease in the absorptance, combined with the removal of the damaged layer and the residue from the conventional polishing, should result in mirrors with a higher laser damage threshold. In fact, Giuliano (ref. 3) has demonstrated that ion polishing of sapphire yielded samples with improved laser damage threshold. Several other studies have also indicated that ion polishing of optical components can produce beneficial results. Bruce and co-workers (ref. 4) have reported that ion polishing of alkali-halide windows resulted in a better surface finish with lower optical absorptance, and we have shown (ref. 5) that ion polishing and overcoating in situ of NaCl yielded windows with improved film adhesion and moisture protection.

The object of the present study was to determine if the ion polishing and annealing techniques used in our previous work could be successfully applied to the polycrystalline metals used for functional laser mirrors. We report here the results of an investigation of the effects of ion polishing and vacuum annealing on the surface finish and absorptance at 10.6 μm of three types of polycrystalline mirror samples: micromachined copper, conventionally polished OFHC copper, and molybdenum.

The extension of these techniques to polycrystalline material is not trivial since the sputtering yields are different for crystallites of different crystallographic orientations which could lead to surface roughening. Our preliminary work on ion polishing of polycrystalline copper and work reported by Willingham (ref. 6) on ion polishing of polycrystalline ZnSe and CaF_2 indeed indicate that differential crystallite sputtering is a problem. In addition, vacuum annealing of polycrystalline material may result in roughening of the surface because of grain growth or thermal etch. Thus it can be expected that the ion polishing parameters, including the amount of material removed as well as the vacuum annealing conditions, will be more critical for polycrystalline material than for single crystal samples.

II. EXPERIMENTAL PROCEDURES

A. Ion Polisher

The ion polishing apparatus was constructed to provide an experimental laboratory facility for removing material from surfaces in a controlled manner. The apparatus, which is fully described elsewhere (ref. 2), is shown schematically in figure 1, along with typical operating conditions. Briefly, the polisher employs sputtering by a focused beam of relatively low energy Xe ions incident on the sample surface at glancing angle, 12° from the plane of surface. The beam is rastered across the surface while the sample is rotated to produce uniform removal of material. The combination of low ion energy, glancing angle of incidence, rastering, and sample rotation are expected to produce a smoothing of the surface features while minimizing damage to the surface. Under these conditions the penetration depth of ions into the sample is estimated from theory (ref. 7) to be ~ 10 Å. Figure 2 depicts the sample chamber of the ion polisher in the configuration for depositing overcoating films. Shown in the figure are a basket evaporation source with shutter, a quartz crystal film thickness monitor, a neutralization filament used when polishing insulating samples, and a phosphor screen used for focusing and positioning the ion beam. In practice, ion polishing at a low removal rate is continued during film deposition to minimize contamination at the interface and in the film, while sample rotation provides better film thickness uniformity over the sample. The removal rate for a given sample type is determined in a separate, calibration run in which the ion polisher is operated at pre-selected conditions. The sample of the particular material is partially masked and, after a known exposure to the ion beam, is removed to determine the step height using a profilometer.

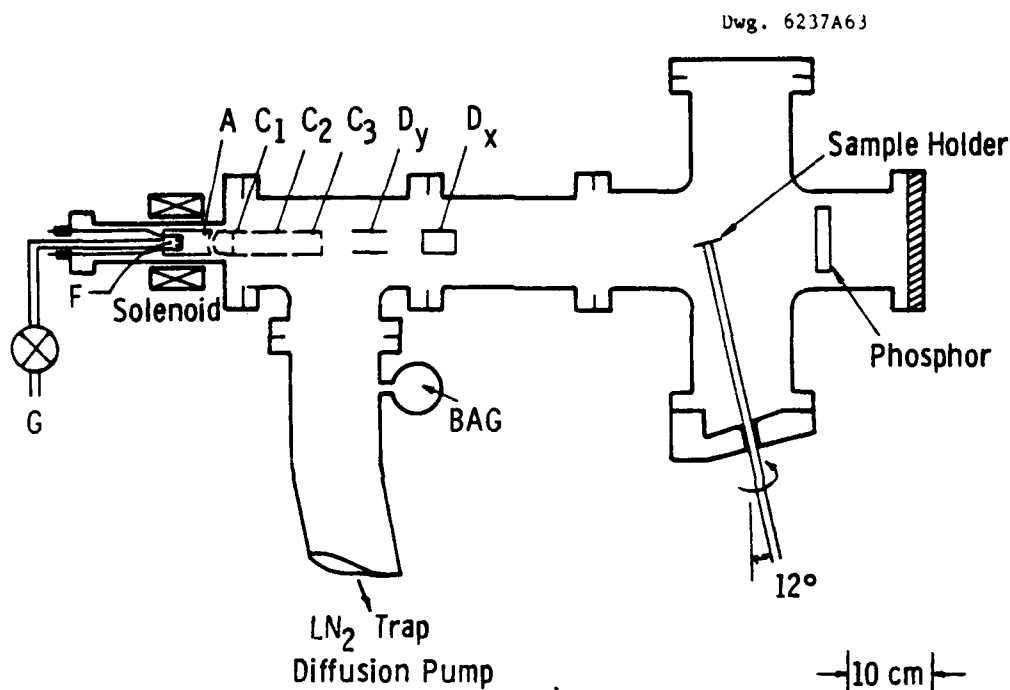


Figure 1. Ion polishing apparatus. The vacuum envelope, except for the large glass cross on the right, is stainless steel at ground potential. The LN₂-trapped, oil diffusion pump provides a base pressure measured by the ion gauge (BAG) of $\leq 5 \times 10^{-8}$ Torr (6×10^{-6} Pa). The system is inclined to the horizontal at 12° , so that the sample is held on the rotatable holder by gravity alone. Electrons supplied by the filament, F, maintain a discharge in the anode, A, into which gas, G, is admitted to maintain a pressure of $\sim 1 \times 10^{-3}$ Torr, some 500 times that in the remainder of the system. Cylinders C₁, C₂, and C₃ comprise the ion lens. Two pairs of plates, D_x and D_y, provide deflection of the beam in the x and y directions; for rastering, frequencies of 1000 and 50 Hz, respectively, are used on D_x and D_y. Typical operating conditions using Xe as the sputtering gas are: filament at +3975 V, anode at +4000 V, C₁ at -2000 V, C₂ at +2600 V, C₃ at ground, target at ground, ion current 10 μ A, sample rotated at 6 rpm.

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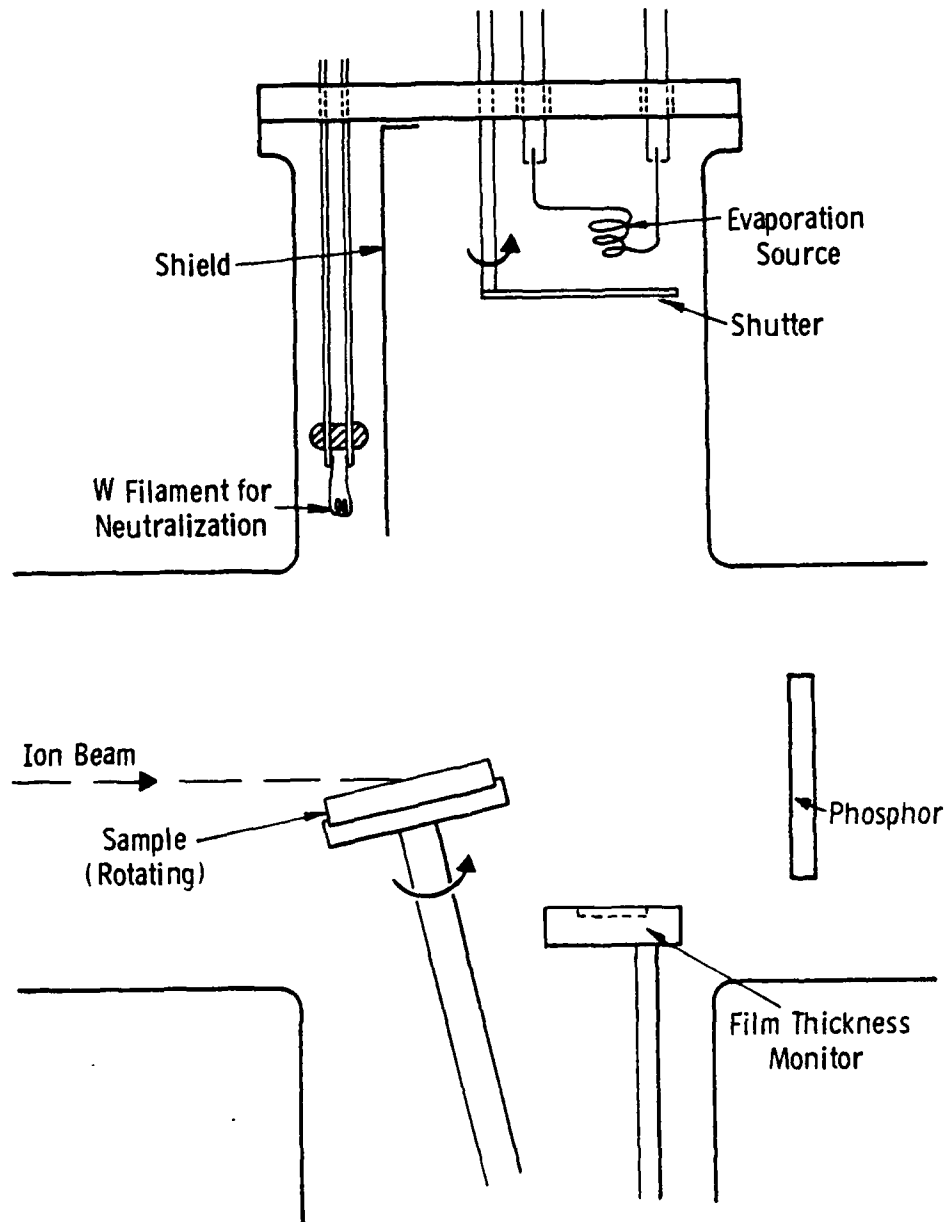


Figure 2. Apparatus for depositing overcoating films in ion planer.

B. Other Apparatus

Since relatively small changes in the sample reflectivity with the various methods of surface preparation are to be expected, it was clear that measurement of absorptivity should be done using optical calorimetry. The calorimeter employed in this study uses a thermal equilibrium technique with substitutional electrical calibration and is fully described elsewhere. After extensive error analysis and experiment, we find that we are able to measure mirrors having an absorptance of 0.01 at a wavelength of 10.6 μm , with a precision of $\leq 1.4\%$ and a systematic error of $\leq 1.6\%$ of the measured value (ref. 8).

Two microscopes were used in this study to examine the sample surfaces to determine the effects of ion polishing and vacuum annealing on surface features. One is a Leitz Ortholux optical microscope with an interference contrast attachment and magnification up to 500X, and the other is a scanning electron microscope (SEM) having magnification up to 20,000X (Materials Analysis Co., Model SX-II). The optical microscope, by virtue of the interference contrast feature, is very sensitive to changes in height on the sample surface; the SEM is relatively insensitive to height differences, due to its large depth of focus, but readily exhibits differences in surface composition.

C. Sample Preparation

Nine 1-1/2 in. diam. sample mirrors consisting of three each of micromachined copper, conventionally polished OFHC copper, and molybdenum were provided by Air Force Weapons Laboratory for use in this study. In order to have enough samples for the various phases of the study, the large mirrors were cut into three 5/8 in. diam. disks (and three irregularly shaped pieces), which incidentally also provided samples of a more convenient size. After the samples were cut by electric discharge machining, they were subjected to ultrasonic cleaning in trichloroethylene, acetone, and methyl alcohol.

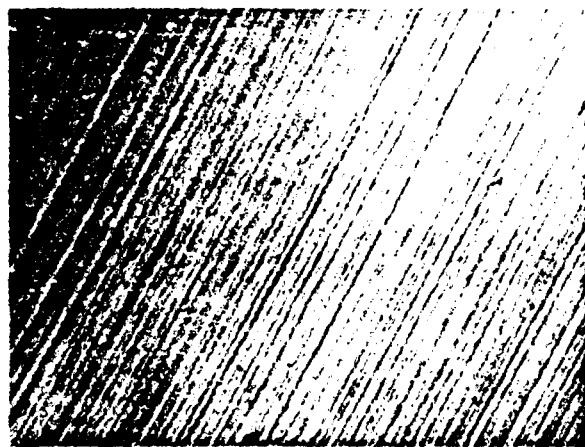
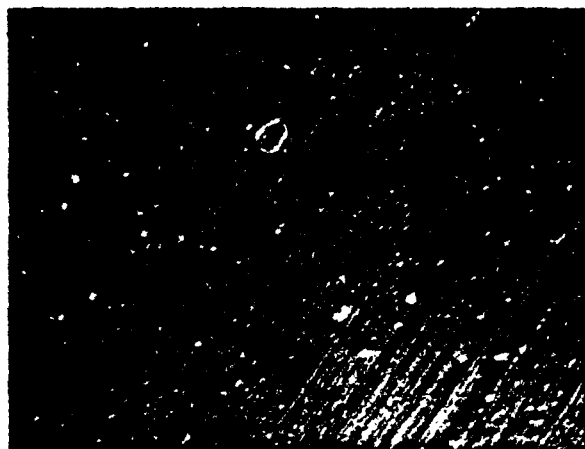
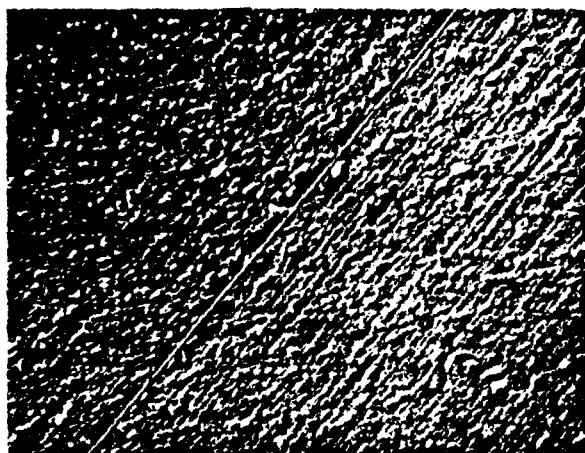
III. RESULTS OF ION POLISHING AND ANNEALING SEQUENCE

A. Micromachined Copper Samples

1. Preliminary Studies

The surface of a 1-1/2 in. diam. micromachined copper sample was examined with the interference contrast microscope and the SEM before it was cut into the smaller samples for subsequent study. Figure 3 shows interference contrast micrographs at three different locations across a diameter of the large, as-received sample, i.e., left hand picture at one edge, center picture in the center of the sample, and right hand picture at the other edge. In addition to the machining marks, other surface features, which are pits, can be observed with varying density over the surface. The pits can be related to ultrasonic cleaning which is discussed more fully in Section IV-C. The pits were seen in the SEM but the machining marks could not be observed with this instrument because the SEM, unlike the interference contrast microscope, has a large depth of focus.

One of the 5/8 in. diam. samples cut from the larger micromachined copper sample was sequentially ion polished and examined with the interference microscope at each stage to determine the progressive effect of ion polishing on the surface features. The results are shown in the interference micrographs of figure 4. The large blemish in the upper right hand corner of the first photograph was a brown spot on the sample which was visible to the unaided eye. This spot was completely removed after the first polishing step, 0.14 μm removed, and the exact spot could not be located again. However, the rest of the pictures in the sequence were taken at the same area near the original spot. Except for the removal of the large blemish, there was no noticeable change in the surface after the first ion polishing step. After the second ion polishing step, total of 0.39 μm removed, the machining marks appeared



100 μ m

Figure 3. Interference contrast micrographs of three areas of the surface of an as-received micromachined copper sample.

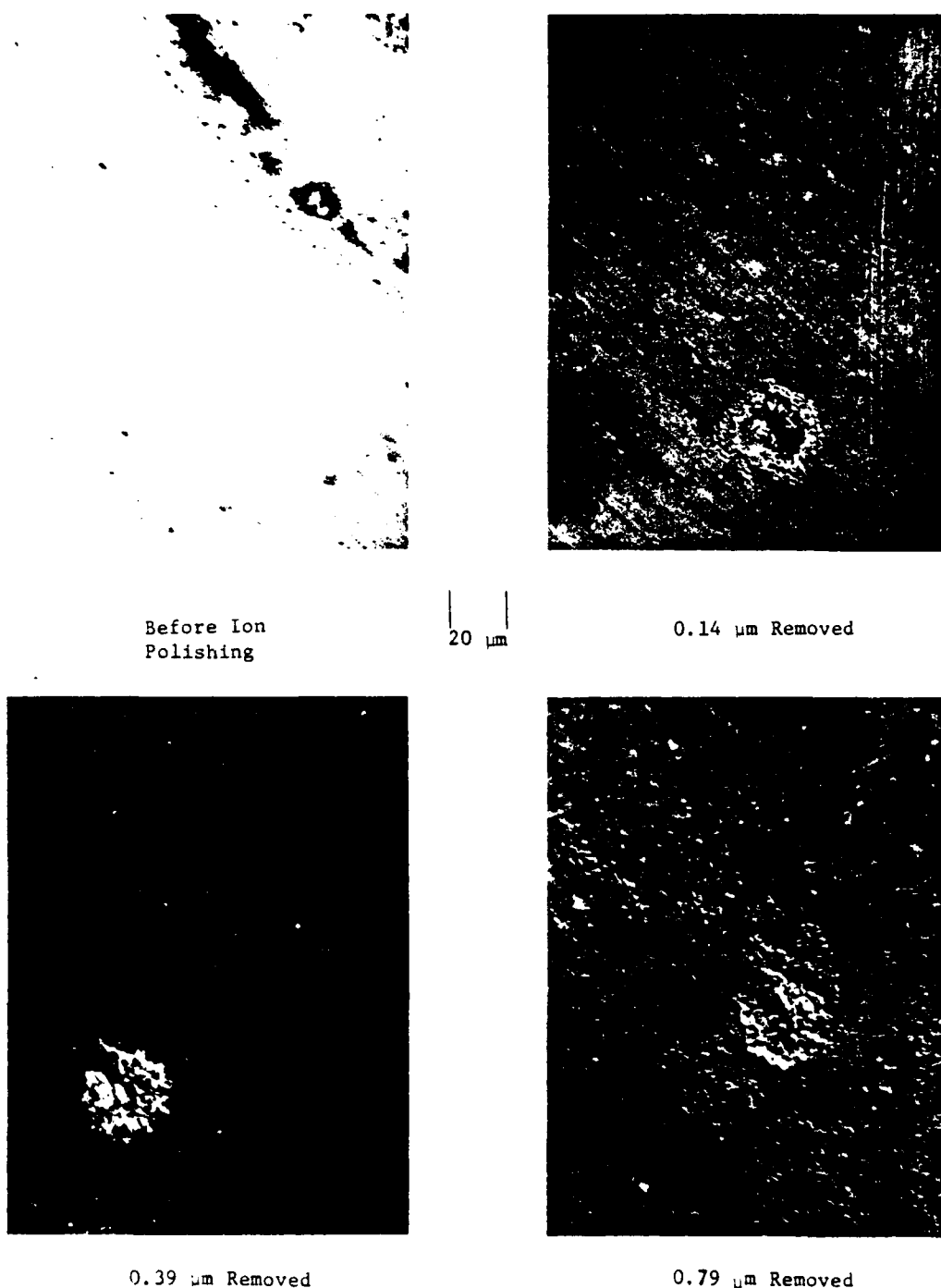
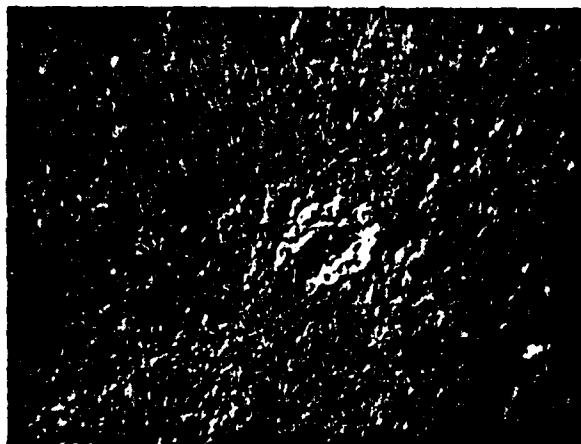
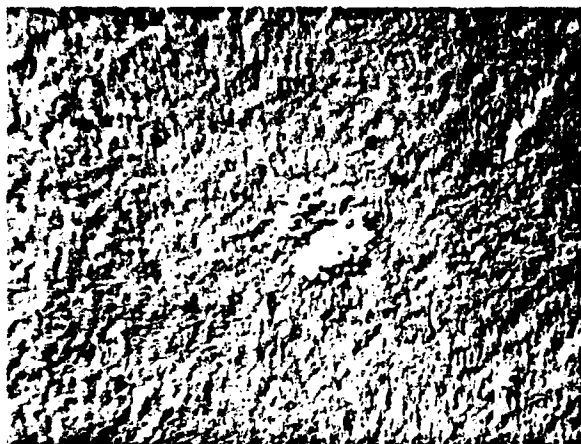


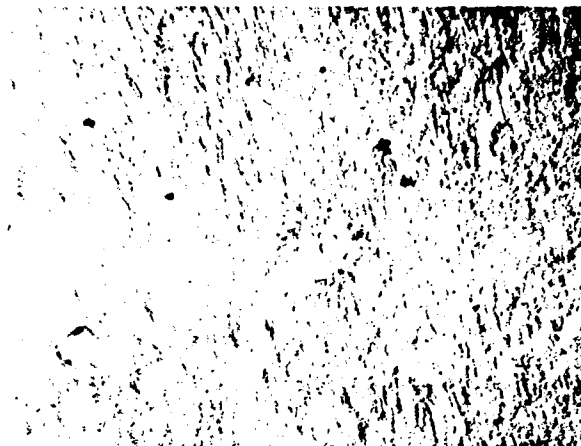
Figure 4. Interference contrast micrographs of micromachined copper after various amounts were removed by ion polishing.



1.19 μm Removed



1.89 μm Removed



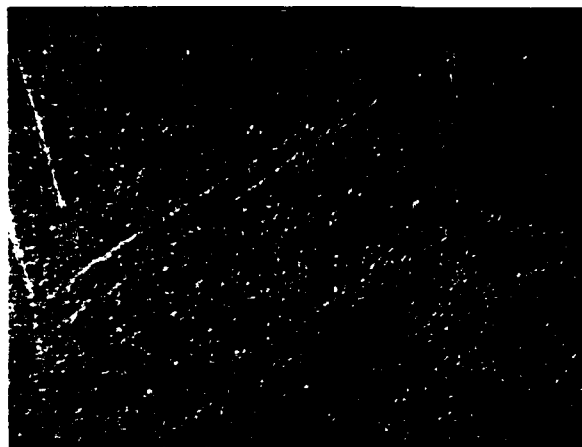
2.49 μm Removed

20 μm

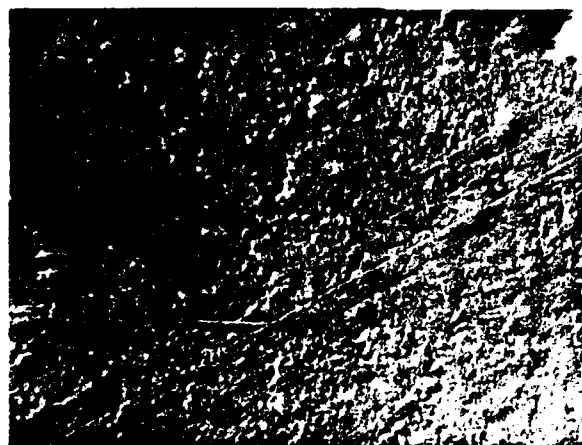
Figure 4. (cont.)

less distinct, and there was a slight trace of some structure in the sample background. As the ion polishing was continued, the machining marks and other blemishes were removed, and the grain structure of the background was enhanced. This is presumably due to the fact that crystallites with different crystallographic orientations, and hence different sputtering yields, are removed at different rates by the ion polishing producing the observed structure. For large amounts of material removed, 1.9 μm or greater, the surface had a practically uniform structure which appeared as a haze to the unaided eye. It is thus concluded that as far as surface structure is concerned, there is an optimum amount to be removed by ion polishing, probably between 0.25 and 0.5 μm , which will remove most of the surface blemishes and yet not significantly roughen the background due to differential crystallite sputtering.

It was also observed that the grain structure of the sample surface revealed during the ion polishing sequence was variable over the sample surface and was vastly different than that observed in previous work on ion polishing of polycrystalline OFHC copper. This is illustrated in figure 5 which consists of interference contrast micrographs of two areas of a micromachined copper sample and of an area of a conventionally polished OFHC copper sample; both samples were ion polished to remove about 7500 Å. The portion of the micromachined copper surface shown in the left hand photograph had a very fine, barely resolvable, grain structure, while the area of the same micromachined sample shown in the center photograph had larger, irregularly shaped grains, some 10-20 μm in diameter. It was also observed that the fine grained area had fewer large defects, as observed with the microscope at lower magnification, than the area with the larger grain size. Both of these areas had very much smaller grains than the conventionally polished OFHC copper sample shown in the right hand photograph which showed crystallites with dimensions of 100-200 μm , some with at least one straight side. Not much is known of the history of the micromachined samples except that information from AFWL indicated that they are OFHC copper and do not have an electroplated copper layer as is normally associated with micromachined samples.

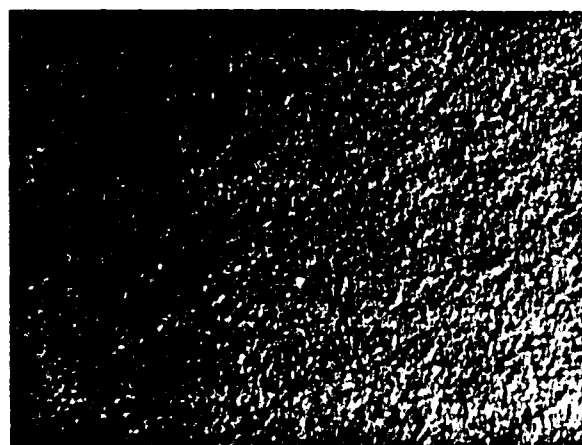


OFHC Cu



Micromachined Cu

20 μ m



Micromachined Cu

Figure 5. Interference contrast micrographs showing the difference in grain structure for micromachined and conventionally polished copper after about 7500 A were removed by ion polishing.

A last minute finding, Section IV-B, shows that the micromachined samples do have a fine-grained copper layer, about 10 mils thick, deposited on a tough pitch copper substrate. More discussion on the differences in grain structure between the micromachined and conventionally polished copper samples is included in Section IV-B in which the study of sample microhardness versus annealing is described.

2. Optimization of Annealing Conditions

A study of the vacuum annealing conditions for the micromachined copper samples was carried out because we interpreted comments from AFWL to suggest that the layer of electroplated copper, usually deposited before micromachining, blisters and starts to peel after a 150°C vacuum anneal and because the annealing temperature that we used in our single crystal copper study was 450°C. (At the time of the annealing study, the first task on this project, we believed that the micromachined samples did have an electroplated copper layer. This, in fact, turned out to be true, see Section IV-B, although after completing the annealing work we were mistakenly told that no electroplated layer was present on these samples). A micromachined copper sample was subjected to one hour vacuum annealing steps at 200°, 325°, 450°, and 600°C with surface examination at each stage using the interference contrast microscope. The results are shown in figure 6 which contains interference micrographs of the sample surface before annealing and after annealing at 325°C, 450°C, and 600°C. A photograph of the surface after the 200°C anneal is not included since it appears to be identical to the initial surface. It is seen that the surface appears to be slightly rougher, possibly due to grain growth or thermal etching after the 325°C anneal and looks progressively worse with higher annealing temperature. The only change in the sample that was visible to the unaided eye was that the surface appeared to be wavy after the 600°C anneal. We had previously found for single crystal copper that vacuum annealing at 200°C did not change the absorptance, but annealing at 450°C did significantly reduce the absorptance after ion polishing. Therefore, it was decided to try an annealing temperature of 325°C to minimize the roughening of the surface and still obtain some beneficial effect on the absorptance. The effect of vacuum annealing on surface structure is also discussed in connection with the microhardness versus annealing study in Section IV-B.



Before anneal

20 μ m



600°C



325°C



450°C

Figure 6. Interference contrast micrographs of micromachined copper after vacuum anneal at various temperatures for one hour.

3. Sequence of Surface Preparation and Absorptance Measurement

After completing the preliminary studies, we were prepared to start the sequence of surface preparation--absorptance measurement--surface examination on the micromachined copper samples. At each stage of the sample surface preparation, i.e., either ion polishing or annealing, the absorptance at $10.6\ \mu\text{m}$ was measured calorimetrically, and the surface was examined using both the interference contrast microscope and the SEM. The results for the absorptance measurements are shown in table 1. The value of the absorptance for the "as-received" sample, which in fact was measured after it was cut from the larger sample and cleaned in the ultrasonic cleaner, is considerably higher than the value determined at AFWL by a reflectivity measurement, i.e., the figure in parentheses. This discrepancy is discussed more fully in Section IV-C dealing with the ultrasonic cleaning study. Referring to the table, the absorptance increased significantly from 0.924% to 1.093% after the first ion polishing (2660 Å removed) and then decreased after vacuum annealing to 0.882%, a value that was less than the original value. This phenomenon of an increase in absorptance with ion polishing and the subsequent net decrease upon annealing to a value below that prior to ion polishing was also observed in our previous work on ion polishing of single crystal copper (ref. 2), where it was speculated that the increase in absorptance following ion polishing was due either to xenon gas ions used in the polishing, which were embedded in the sample surface, or to a damage layer at the sample surface caused by the bombarding xenon ions. By annealing the single crystal copper samples in a system equipped with a mass spectrometer, it was determined that most of the trapped xenon gas was released during annealing at 200°C but that there was no decrease in absorptance after such an anneal. The decrease in absorptance was observed after the 450°C anneal. We thus concluded that for the single crystal copper samples the increase in absorptance after ion polishing was due to surface damage caused by the bombarding gas ions which was annealed out by heating to 450°C in vacuum. It is believed that a similar explanation holds for the present samples and that heating to 320°C for 1-1/4 hours is sufficient to anneal out the damage caused

TABLE 1
ABSORPTANCE OF MICROMACHINED COPPER AT VARIOUS STAGES
OF SURFACE PREPARATION

Sample Preparation	Absorptance
R = 99.21%, measured at AFWL	(0.79%)
As received	0.924%
Ion polished, 2660Å removed	1.093%
Vacuum annealed, 320°C, 1-1/4 hours	0.882%
Ion polished, 2080Å removed, 4740Å total	0.895%
Vacuum annealed, 320°C, 1-1/4 hours	0.866%
Ion polished, 1850Å removed, 6590Å total	0.944%
Vacuum annealed, 325°C, 1-1/4 hours	0.914%
Ion polished, 2490Å removed, 9080Å total	0.849%
Vacuum annealed, 320°C, 1-1/4 hours	0.794%
Ion polished, 2890Å removed, 11,970Å total	0.888%
Vacuum annealed, 320°C, 1-1/4 hours	0.820%

by the bombarding xenon ions. Note that annealing at 320°C was not tried in the previous study on single crystal copper.

Referring to table 1, another complete cycle of ion polishing (2080 Å removed with 4740 Å total removed) and vacuum annealing reduced the absorptance from 0.882% to 0.866%. Continuing the ion polishing and vacuum annealing further yielded mixed results, i.e., after two of the polishing-annealing cycles, the absorptance increased, and after one cycle, the absorptance decreased significantly. It is believed that the observed changes are real and meaningful and not due to uncertainty in the measurement (see Section II-B) or to probing different portions of the sample mirror, since each cycle involves two measurements, i.e., after ion polishing and after annealing, which correlate well. When the value of the absorptance is high after ion polishing, it is also high after annealing, and conversely when one is low the other is also. It should be noted that the sample must be physically removed and remounted for each of the measurements; the remounting is done by visually judging the center of the sample using an alignment laser. At present, there is no satisfactory explanation for these results except that one might expect higher values for the absorptance when large amounts of material are removed and the surface becomes roughened due to differential sputtering of the crystallites.

Figure 7 shows interference contrast micrographs of the micromachined copper sample at the various stages in the surface preparation sequence. A significant change in the appearance of the surface occurred after the first vacuum anneal at 320°C. Because no detectable change in the surface occurred following subsequent annealing, these pictures are not included in the figure. Figure 8 contains similar photographs for another region of the surface of the same sample and shows a smaller grain structure. Referring to figures 7 and 8, it is seen that the first ion polishing step (2660 Å removed) eliminated most of the major blemishes and reduced the visibility of the machining marks. A suggestion of grain structure can be seen, particularly in figure 7b. The first annealing, 320°C for 1-1/4 hours, enhanced the grain structure further (Figs. 7c and 8c) as was seen in the annealing study. The machining marks were almost



a) Before Ion
Polishing

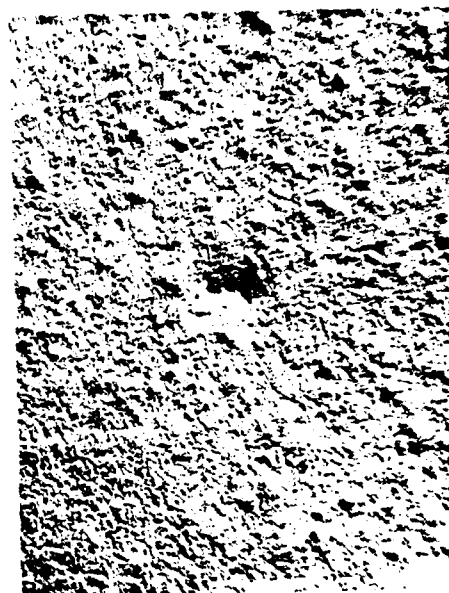


b) 2660 Å Removed

20 μ m

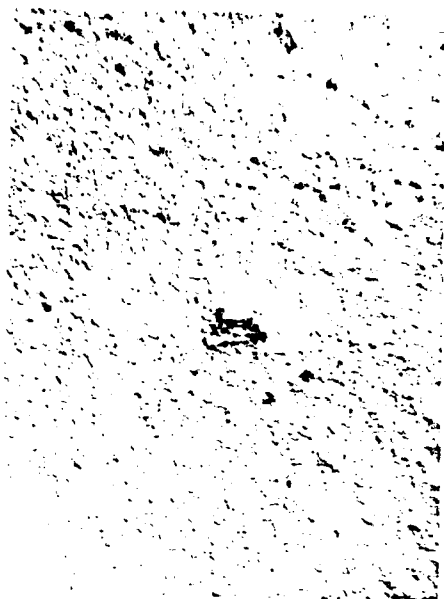


c) 320°C Anneal

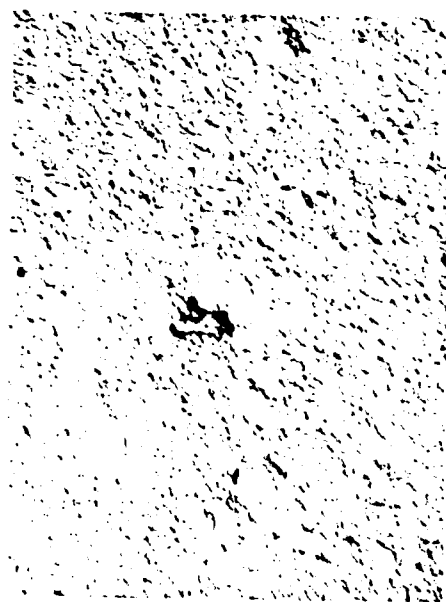


d) 4740 Å Removed

Figure 7. Interference contrast micrographs of micromachined copper at various stages in the ion polishing and vacuum annealing sequence.

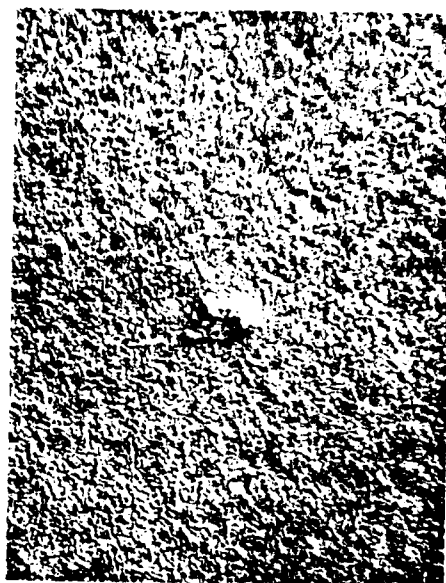


e) 6590Å Removed



f) 9080Å Removed

20 μm



g) 11,970Å Removed

Figure 7. (cont.)

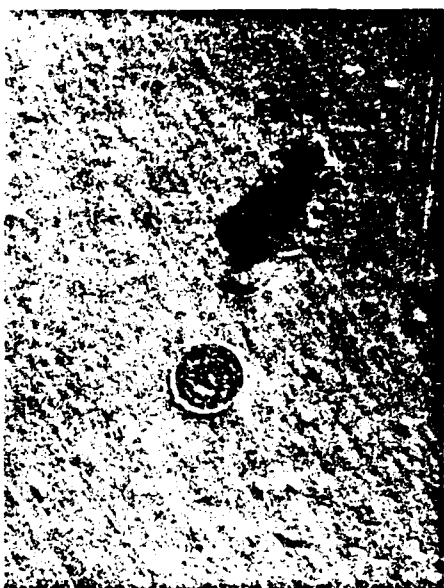


a) before Ion
Polishing

20 μ m



b) 2660Å Removed

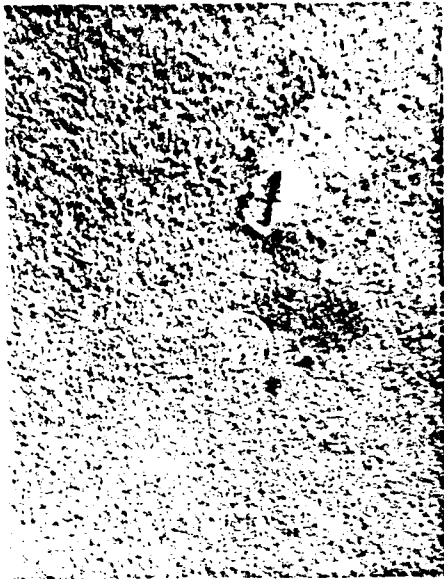


c) 320°C Anneal

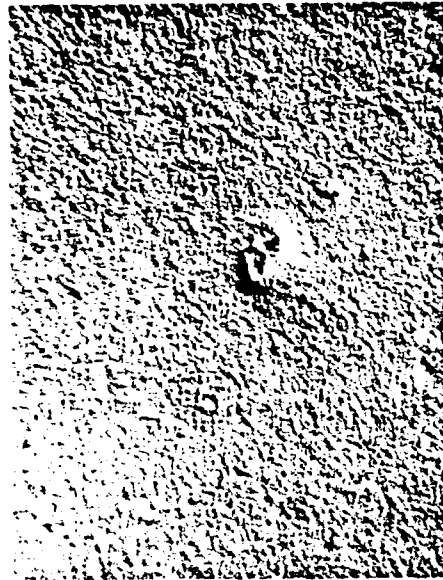


d) 4740Å Removed

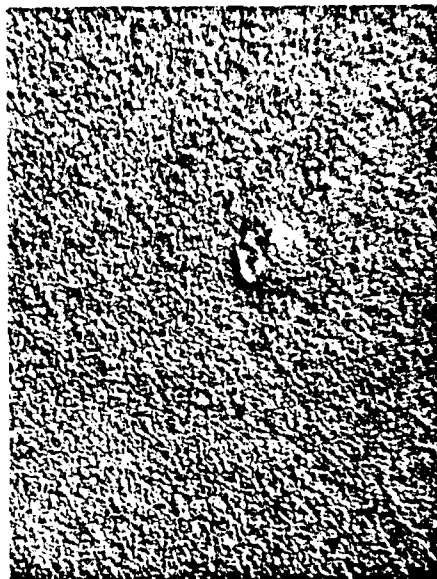
Figure 8. Interference contrast micrographs of micromachined copper at various stages in the ion polishing and vacuum annealing sequence.



e) 6590Å Removed



f) 9380Å Removed



g) 11,970Å Removed

Figure 8. (cont.)

completely eliminated, and the blemishes further reduced by the second ion polishing step (2080 Å removed with 4740 Å total removed). See figures 7d and 8d. Continuing the sequence resulted in further crystallite delineation and a roughened surface. For example, after 9080 Å were removed, the surface appeared slightly hazy to the unaided eye and was worst in the fine grained area which scattered the He-Ne alignment laser noticeably. It should be noted, however, that the measured absorptance, 0.794%, was very low.

Figure 9 shows SEM micrographs of the sample at the same stages of surface preparation, although the various photographs were not necessarily taken at the identical position each time. The initial surface was featureless except for a few pits. A trace of the grain structure can be seen after the first ion polishing step (Fig. 9b), probably because the damage layer caused by the machining operation has been removed, or partially removed, by the ion polishing--thus revealing the crystal line structure of the substrate. The grain structure is seen more clearly after the first anneal (Fig. 9c), due to either surface recrystallization or thermal etch. Figure 9 shows, as did the two previous figures, that for large amounts of material removed by ion polishing, i.e., greater than 5000 Å, the grain structure is enhanced and the surface roughened.

4. Conclusions

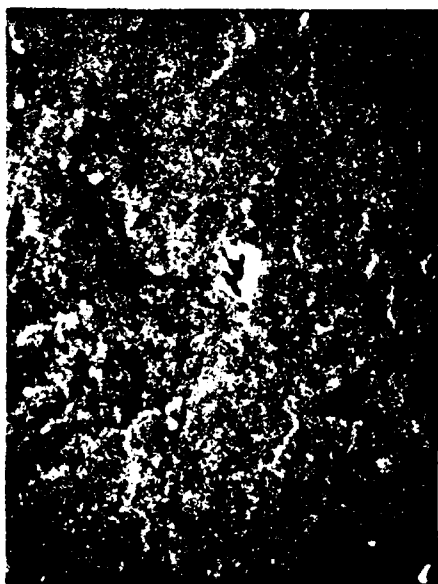
It is concluded that for the micromachined copper sample studied here, the combination of ion polishing and vacuum annealing results in a small decrease in the absorptance, 5-10% of the initial value, at a wavelength of 10.6 μm. It should be noted, however, that the micromachined copper samples initially have low absorptance, 0.92%, and there is not much room for improvement since the lowest value we have measured for copper (an ion polished, pure, single crystal) is 0.76%. It is also concluded, from examination of the surface micrographs, that there is an optimum amount of material to be removed by ion polishing, which will remove all but the largest blemishes, and yet not produce significant roughening due to differential sputtering of the crystallites.



a) Before Ion Polishing



b) 2660Å Removed

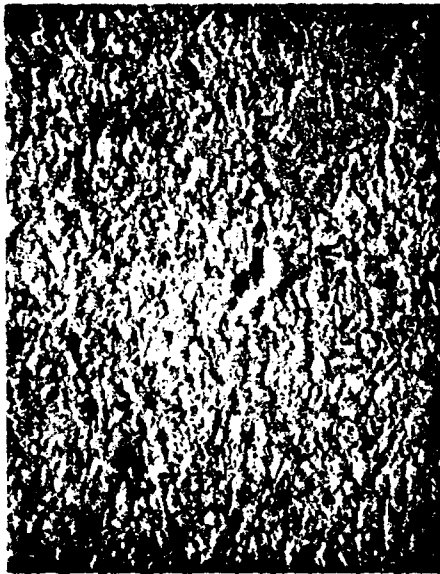


c) 320°C Anneal

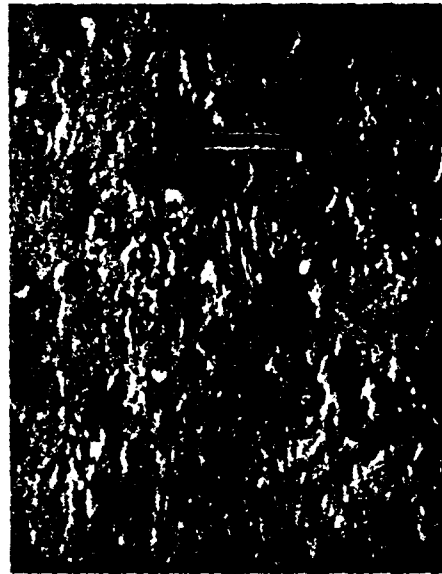


d) 4740Å Removed

Figure 9. SEM micrographs of micromachined copper at various stages in the ion polishing and vacuum annealing sequence.



e) 6590A Removed



f) 9080A Removed

5 μ m



g) 11,970A Removed

Figure 9. (cont.)

The optimum amount for the micromachined copper samples studied lies between 0.25 and 0.5 μm . The removal of residue and blemishes from the sample surface may be a significant benefit in raising the laser damage threshold and in improving thin film coating adhesion in these samples.

It is interesting to note that there does not seem to be a correlation between surface roughness and absorptance in the samples studied. The lowest value measured for the absorptance, 0.79%, was obtained after about 9000 $\text{\AA}$ had been removed from the sample, yet the surface was significantly roughened. It is also observed that after ion polishing, a sample which has been annealed is roughened more than one which has not been annealed, even though approximately the same amount is removed. This is reasonable since it is expected that the surface layer has been damaged by the micromachining operation and that the damaged surface will sputter more uniformly than a crystalline surface and result in a minimum of surface structure. For an annealed sample, it can be expected that the surface is recrystallized, thus showing grain enhancement effects associated with the different sputtering rates of crystallites of different orientations. Thus, the preferred sequence for ion polishing and annealing to obtain minimum absorptance and minimum surface roughness is to remove only the damaged surface layer by ion polishing in one step and then to vacuum anneal the sample. A further discussion on ways to minimize effects of differential sputtering appears in the final section of the report.

B. Conventionally Polished Copper Samples

1. Sequence of Surface Preparation and Absorptance Measurement

The sequence of surface preparation--absorptance measurement--surface examination was initiated on the conventionally polished OFHC copper samples using the same ion polishing and vacuum annealing conditions determined for the micromachined copper samples. The results for the absorptance measurements are given in table 2. The absorptance of the as-received sample, which again was obtained after it was cut from a larger sample and subjected to ultrasonic cleaning, is significantly higher

TABLE 2

ABSORPTANCE OF CONVENTIONALLY POLISHED COPPER AT
VARIOUS STAGES OF SURFACE PREPARATION

Sample Preparation	Absorptance
R = 98.65%, measured at AFWL	(1.35%)
As received	1.536%
Ion polished, 2290Å removed	0.876%
Vacuum annealed, 320°C, 1-1/4 hours	0.864%
Vacuum annealed, 450°C, 1-1/4 hours (oxidized)	0.862%
Ion polished, 630Å removed, 2920Å total	0.902%
Vacuum annealed, 450°C, 1-1/4 hours	0.866%
Ion polished, 2490Å removed, 5410Å total	0.814%
Vacuum annealed, 450°C, 1-1/4 hours	0.788%
Ion polished, 3160Å removed, 8570Å total	0.848%
Vacuum annealed, 450°C, 1-1/4 hours	0.810%

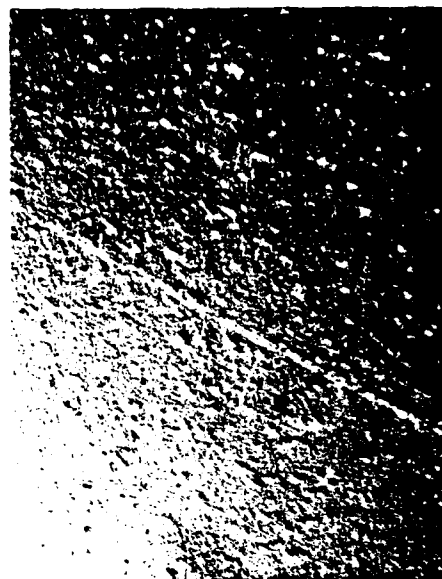
than that measured at AFWL (the value in parentheses) by a reflectivity method. This difference is discussed more fully in Section IV-C on the ultrasonic cleaning study. It is seen that the absorptance decreased dramatically from 1.536% to 0.876% after the first ion polishing step in which 2290 Å was removed. This decrease in absorptance is striking and prompts speculation as to its cause. Perhaps the layer removed by ion polishing was heavily damaged by the conventional polishing, leading to high absorptance or perhaps surface contamination from the conventional polishing was removed by the ion polishing. In support of the latter idea, the sample had a brown tint before ion polishing but appeared bright copper in color after ion polishing. However, if a surface contaminant was present, it was very tenacious since the samples were subjected to ultrasonic cleaning in various solvents prior to the initial measurement. Whatever the reason for the decrease, it should be noted that the absorptance of this conventionally polished sample was reduced to a value as low as that of the micromachined sample. Following the initial ion polishing, the sample was annealed in vacuum at 320°C for 1-1/4 hours. The absorptance decreased slightly but not as much as expected. It was decided to try a higher temperature anneal, 450°C, at which annealing was carried out in our previous, single-crystal copper work. Unfortunately, the sample became slightly oxidized, as seen by the unaided eye, during this annealing because the high vacuum value on the furnace was inadvertently closed leaving the sample only under forepump vacuum during annealing; however, the absorptance did not change as a result of this annealing. Another cycle of ion polishing and annealing was performed on this sample, but only a small amount of material was removed (630 Å) by ion polishing--just enough to remove the oxide film. It is seen that the absorptance did not change after complete cycle although the annealing did produce some benefit after the ion polishing. It can be concluded that the presence of the visible oxide film did not increase the absorptance at 10.6 μm and that annealing at 450°C offers no advantage over annealing at 320°C for these samples, as far as the optical absorptance is concerned.

Continuing the sequence through another cycle of ion polishing and annealing resulted in a decrease in absorptance to 0.788%, a very low value for the absorptance of copper at 10.6 μm . Note, that this value is as low as or lower than the best value for the micromachined samples reported above and is almost as low as our best value for single crystal copper, 0.76% (ref. 2). One more cycle of ion polishing and annealing resulted in an increase in the absorptance to 0.810%, perhaps due to increased surface roughness caused by differential sputtering of the crystallites.

Figure 10 shows interference contrast micrographs of the conventionally polished OFHC copper sample surface at various stages of the sample preparation sequence. The initial surface, which had a brown tint, contained numerous polishing scratches. After the first ion polishing step, in which 2290 Å were removed (Fig. 10b), the surface was a bright copper color, the polishing scratches were partially removed, and there was no evidence of grain structure caused by differential sputtering of the crystallites. Annealing at 320°C for 1-1/4 hours caused some enhancement of the grain boundaries due to grain growth or thermal etching (Fig. 10c). As mentioned previously, the sample surface accidentally became oxidized during the 450°C anneal, and figure 10d shows that various crystallites oxidized differently as a result of the fact that surfaces with different crystallographic orientations form oxides at different rates. Note also that the grain boundaries appear to be enhanced further and that the size and shape of these crystallites are very different from those of the micromachined copper (Figs. 7 and 8). The next ion polishing step (630 Å removed and 2920 Å total) was meant to remove just the oxide layer from the surface, and figure 10e shows this to be the case. The annealing at 450°C after this and subsequent ion polishing steps caused no noticeable change in the surface features, and hence these photographs are not included in the figure.

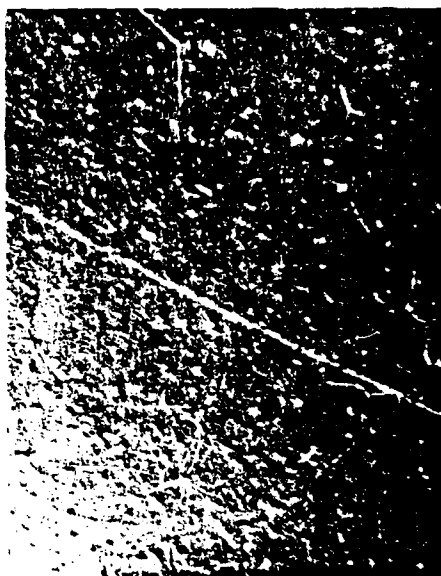


a) Before Ion
Polishing



b) 2290A Removed

100 μ m



c) 320°C Anneal

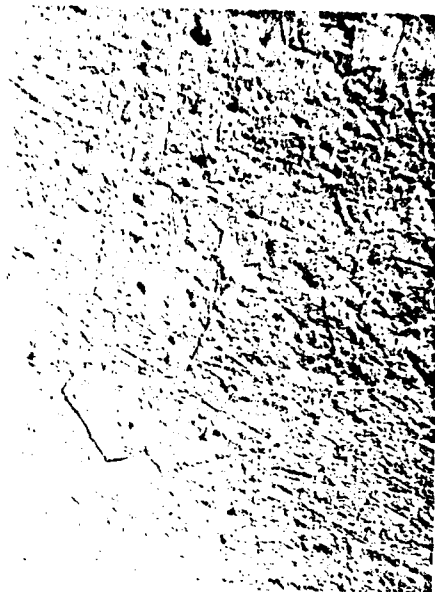


d) 450°C Anneal
(Oxidized)

Figure 10. Interference contrast micrographs of conventionally polished copper at various stages in the ion polishing and vacuum annealing sequence.



e) 2920Å Removed



f) 5410Å Removed



g) 8570Å Removed

Figure 10. (cont.)

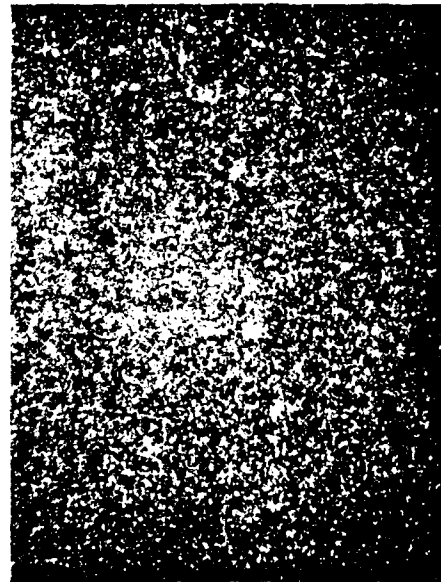
Further ion polishing resulted in an increase in the surface roughness caused by differential crystallite sputtering (Figs. 10f and 10g). After 5410 Å of material was removed, the surface appeared to have an "orange peel" finish and noticeably scattered the He-Ne alignment laser in the calorimeter.

Figures 11 and 12 show SEM micrographs at two different magnifications of the sample at the same stages in the preparation sequence. The photographs at the various stages were not necessarily taken at the same spot on the sample. The "as-received" sample appeared to be electrically charging in the SEM (Fig. 11a). After the first ion polishing step, the charging problem disappeared, and the sample surface appeared to be covered with white spots (Figs. 11b and 12b). It is believed that the white spots were due to particles of polishing grit, which, being dielectric, charge up in the SEM and appear as white spots. It is further postulated that the grit, embedded in the surface during conventional polishing, has a lower sputtering yield than copper and was exposed as the surrounding copper was sputtered at a faster rate. We have observed a similar phenomenon in our previous work with single crystal copper, which was also initially polished using dielectric grit. No such grit was detected in the micromachined copper samples.

The SEM photographs in figures 11 and 12 also show the grain boundary enhancement following the 320°C anneal and the oxidation evident after the 450°C anneal. The differential oxidation rate of various crystallites is strikingly apparent in these photographs since the SEM is very sensitive to compositional differences at the surface. The oxide film was removed by the next ion polishing step (630 Å removed); see figures 11e and 12e. The polishing grit appears to have nearly disappeared after removing 5410 Å by ion polishing and to be completely gone after a total of 8570 Å was removed. The final photographs (Figs. 11g and 12g) also show smoothing of the polishing scratches and enhancement of the grain boundaries.

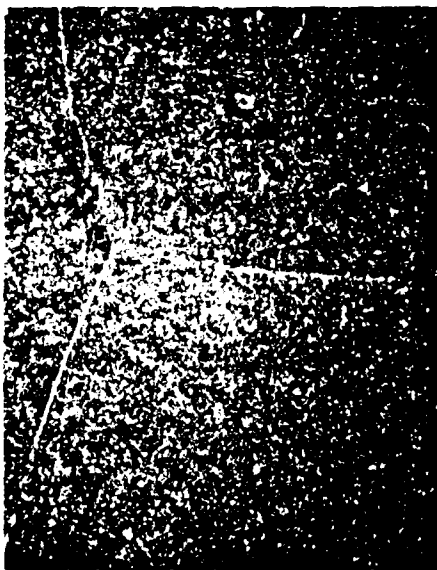


a) Before Ion
Polishing

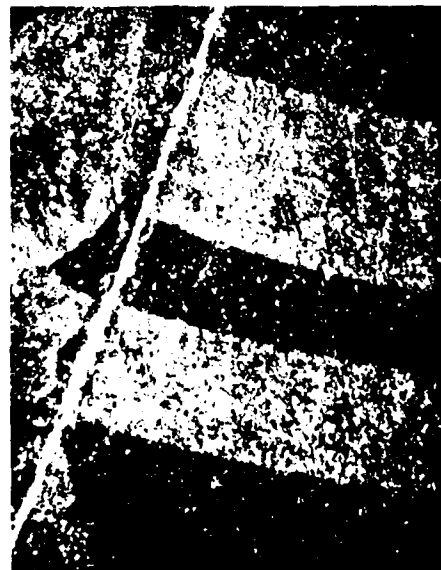


b) 2290 Å Removed

10 μ m

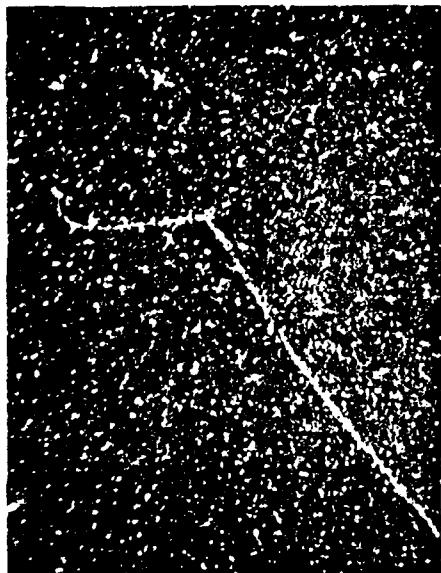


c) 320°C Anneal



d) 450°C Anneal
(Oxidized)

Figure 11. SEM micrographs of conventionally polished copper at various stages in the ion polishing and vacuum annealing sequence.



e) 2920Å[°] Removed



f) 5410Å[°] Removed

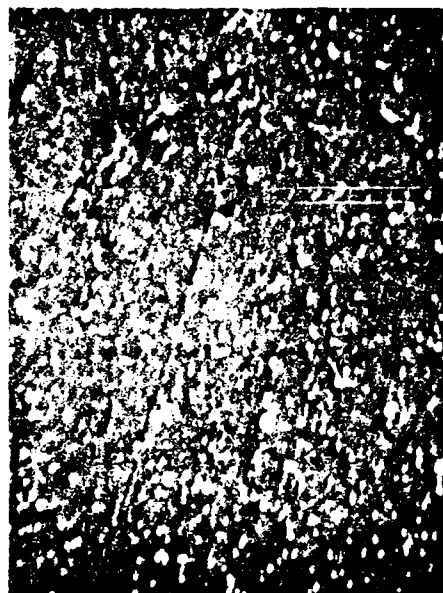


g) 8570Å[°] Removed

Figure 11. (cont.)



a) Before Ion
Polishing



b) 2290Å Removed

2 μ m

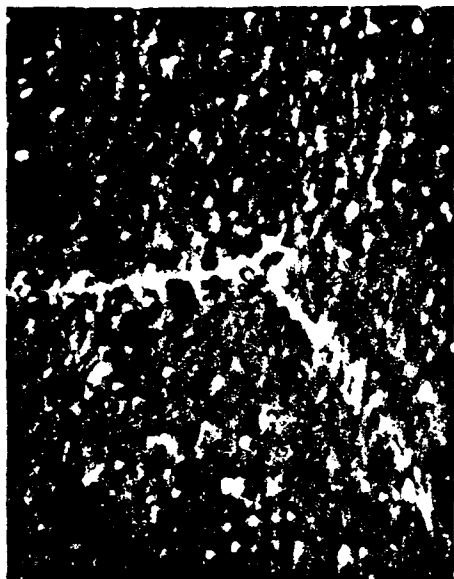


c) 320°C Anneal

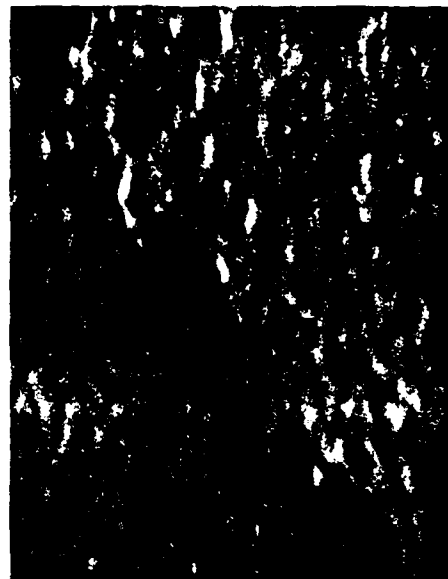


d) 450°C Anneal
(Oxidized)

Figure 12. SEM micrographs of conventionally polished copper at various stages in the ion polishing and vacuum annealing sequence.



e) 2920Å Removed



f) 5410Å Removed

2 μm



g) 3570Å Removed

Figure 12. (cont.)

2. Conclusions

For the conventionally polished samples studied here, it is evident that ion polishing in which only a relatively small amount of material ($2290 \text{ \AA}$) is removed, results in a large decrease in the absorptance, 40-50% of the initial value. This large decrease in absorptance is probably due to the removal by ion polishing of surface contamination. After ion polishing, the conventionally polished samples exhibit an absorptance which is as low as the micromachined copper samples. Vacuum annealing at 320°C for 1-1/4 hours affords a further small decrease in the absorptance but at the expense of increased surface roughness due to grain boundary enhancement. This may not be a problem since it is felt that the annealing conditions for copper are not yet optimized.

Ion polishing reveals the presence of polishing grit used in conventional polishing and embedded in the copper surface. This grit is removed by further ion polishing to remove more than $5000 \text{ \AA}$. Polishing grit embedded in a mirror surface could seriously lower its laser damage threshold, particularly if the grit has appreciable absorptance at the laser wavelength, and its removal is essential for the production of mirrors with consistently high damage thresholds.

As with the micromachined copper samples, there is an optimum amount of material to be removed by ion polishing which will remove contamination, including polishing grit, minimize surface defects such as polishing scratches, and not cause appreciable surface roughness due to differential crystallite sputtering. We conclude that this optimum amount to be removed is $5000\text{-}7000 \text{ \AA}$ for the conventionally polished samples studied. In order to minimize the effects of differential sputtering of the various crystallites, the ion polishing should be completed before the sample is subjected to vacuum annealing since annealing tends to recrystallize the surface and leads to enhanced preferential sputtering. Other possible methods for minimizing the effects of differential crystallite sputtering are discussed in the final section of the report.

C. Molybdenum Samples

1. Optimization of Annealing Conditions

A study to determine the optimum annealing conditions for molybdenum samples was carried out by submitting the test sample to vacuum annealing for one hour at each of several temperatures. After each anneal cycle, the surface was examined using the interference contrast microscope. The results are shown in figure 13. The history of the molybdenum samples prior to being delivered to us was unknown; the micrographs taken before annealing showed a terrace-like structure with very few scratches, giving the appearance of a surface that had been polished by a mechanical-chemical method or had been mechanically polished and then etched. However, in spite of the surface structure shown, it was noted when examining the sample that it exhibited very little scattering of the microscope light. The first anneal, at 800°C for one hour, resulted in no change in the surface features. The next vacuum anneal, 1000°C for one hour, caused some small scale roughening, also shown in figure 13. It was also observed that there was much more scatter of the microscope light by the surface after the 1000°C anneal. The surface micrograph after annealing at 1200°C, which was taken on a different molybdenum sample but cut from the same large sample, shows increased roughening of the background and what appears to be enhancement of the crystallite boundaries. Thus, it is concluded that when annealing molybdenum samples for one hour the temperature should be less than 1000°C, to avoid increased roughness and scatter, and that a good starting point would be annealing at 800°C for one hour.

2. Sequence of Surface Preparation and Absorptance Measurement

The sequence of surface preparation--absorptance measurement--surface examination was then carried out for the molybdenum samples using procedures similar to those employed with the copper samples. With the same ion polishing conditions as were used for the copper samples, a removal rate was established for the molybdenum samples which was about one-third that for copper. This is in agreement with published values



Before annealing

20 μ m
| |



1200°C anneal



800°C anneal



1000°C anneal

Figure 13. Interference contrast micrographs of molybdenum after vacuum anneal at various temperatures for one hour.

for the sputtering yields of molybdenum and copper. The vacuum annealing conditions were fixed at 800°C for one hour. The results of the absorptance measurements at the various stages of surface preparation of the molybdenum samples are given in table 3. Good agreement exists between the absorptance measured for the as-received sample, actually after cutting from the larger sample and ultrasonic cleaning, and the value determined at AFWL by reflectivity, which is given in parenthesis. The absorptance increased from 1.844% to 1.888% after the first ion polishing step (970 Å removed) and then decreased to 1.688% after the first annealing step. The sizable decrease in sample absorptance with annealing suggests that the annealing conditions used were close to optimum. Note that the combination of ion polishing, removing only 970 Å, and vacuum annealing resulted in a significant decrease in absorptance in the molybdenum sample. The second ion polishing step, in which 1780 Å were removed for a total of 2750 Å, resulted in an increase in the sample absorptance while the subsequent anneal resulted in a decrease to 1.673%, slightly less than the value before the second ion polishing. This increase in absorptance after ion polishing, followed by an even larger decrease after annealing, is similar to the behavior observed in the copper samples. As discussed in Section III-A-3, the increase in absorptance is presumably due to damage which is caused by the bombarding xenon ions and which is subsequently annealed out to yield an overall decrease in the absorptance. Another cycle of ion polishing (2520 Å removed with 5270 Å total removed) and annealing resulted in a further small decrease in the sample absorptance to 1.660%.

Interference contrast micrographs of this molybdenum sample at the various stages of surface preparation are shown in figure 14; since there was no detectable change in the surface after any of the annealing steps, these micrographs are not included. The initial surface, shown in figure 14a is characterized by a terraced structure with some remnant scratches and, as described above, is attributed to mechanical-chemical polishing or mechanical polishing followed by etching. The surface was not greatly changed after the first ion polishing step (Fig. 14b), as might be expected, since only 970 Å were removed; however, it appears as

TABLE 3

ABSORPTANCE OF MOLYBDENUM AT VARIOUS
STAGES OF SURFACE PREPARATION

Sample Preparation		Absorptance
#I	R = 98.11%, measured at AFWL	(1.89%)
	As received	1.844%
	Ion polished, 970Å removed	1.888%
	Vacuum annealed, 800°C, 1 hour	1.688%
	Ion polished, 1780Å removed, 2750Å total	1.895%
	Vacuum annealed, 800°C, 1 hour	1.673%
	Ion polished, 2520Å removed, 5270Å total	1.855%
	Vacuum annealed, 800°C, 1 hour	1.600%
#II	R = 98.11%, measured at AFWL	(1.89%)
	As received	1.897%
	As received, remeasured	1.907%
	Vacuum annealed, 800°C, 1 hour	1.715%



a) Before Ion
Polishing

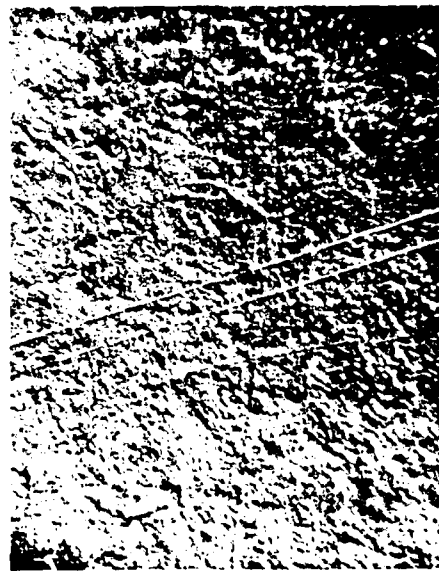


b) 970A Removed

20 μ m



c) 2750A Removed



d) 5270A Removed

Figure 14. Interference contrast micrographs of molybdenum at various stages in the ion polishing and vacuum annealing sequence.

if the fainter scratches were partially removed. After the second ion polishing cycle (1780 Å removed or 2750 Å total) pits in the surface are evident (Fig. 14c) and result in considerable scattering of the microscope light and He-Ne alignment laser. The final ion polishing step (2520 Å removed with 5270 Å total removed) further reduced the original surface blemishes, however the pitting of the surface was much worse and there was some evidence of grain boundary enhancement due to differential crystallite sputtering (Fig. 14d).

The SEM micrographs of the molybdenum sample at the same stages of surface preparation (Fig. 15) show essentially the same features. Initially, only the grain structure of the surface can be seen while as more material is removed by ion polishing the pits develop. No evidence of polishing grit in the surface, as was seen on the conventionally polished copper sample, appears in the SEM micrographs. One can speculate as to the cause of the pitting of the molybdenum surface with ion polishing, e.g., latent features of the material which derive from a powder metallurgy technique used in producing the molybdenum initially. Perhaps the pits occur where voids in the material exist and are revealed by the ion polishing. Alternatively, the pits may result from the presence of a second phase in the material which has a higher sputtering yield and is removed faster. Whatever the cause, the presence of such imperfections in the material near the surface could seriously influence the laser damage threshold of the mirror.

Since vacuum annealing had such a large effect on the absorptance of the molybdenum sample after ion polishing, it was decided to prepare a sample using such annealing without ion polishing. The molybdenum sample used was cut from the same large disk as the sample discussed previously. The results are given in table 3, sample #II. Initially the absorptance was measured and the sample removed from the calorimeter, remounted, and the absorptance remeasured. It is seen that excellent agreement exists between the two measured values and also with the value determined at AFWL. The sample was then vacuum annealed (800°C for 1 hour) resulting in a significant decrease in the absorptance, about 10% of the initial value. No change was detectable in the sample surface after annealing, using either the interference microscope or the SEM.



a) Before Ion
Polishing



b) 970 Å Removed

2 μm



c) 2750 Å Removed



d) 5270 Å Removed

Figure 15. SEM micrographs of molybdenum at various stages in the ion polishing and vacuum annealing sequence.

3. Conclusions

Suitable conditions were determined for annealing molybdenum mirrors which result in significant decrease in the absorptance at a wavelength of 10.6 μm , about 10% of the initial value, and yet do not change the surface features. The annealing conditions are 800°C under vacuum for one hour. The combination of ion polishing and vacuum annealing results in a further small decrease in the absorptance and partially removes blemishes on the sample surface for small amounts, ≤ 1500 Å, of material removed. For larger amounts of material removed by ion polishing, the surface becomes pitted, causing increased scattering of light. Grain boundary enhancement, caused by differential sputtering of the crystallites, also appears when larger amounts of material are removed. It is believed that the cause of pitting has its origin in the original processing of the molybdenum substrate material and that means should be sought to eliminate it since imperfections in the molybdenum near the mirror surface could significantly lower its laser damage threshold.

IV. OTHER RESULTS

A. Auger Analysis and Coating Study of Ion Polished Copper Samples

During discussions with AFWL personnel, it became apparent that a major problem with micromachined copper mirrors, as contrasted with conventionally polished ones, is the poor and inconsistent adhesion of dielectric films to micromachined substrates (ref. 9). It is highly desirable to be able to deposit a system of multilayer dielectric films on micromachined copper mirrors to enhance their reflectivity, especially if the mirrors are to be used at laser wavelengths shorter than 10.6 μm where the reflectivity of copper is lower. At present, no satisfactory explanation exists for the poor adherence of films to micromachined copper substrates, but several possible reasons include: surface contamination from the micromachining operation, surface strain due to the inherent cold working associated with the machining process, or the unusual grain structure of the micromachined surface (already noted in Section III-A1).

It was decided to prepare several samples of each type of material, i.e., micromachined copper and conventionally polished OFHC copper, using combinations of ion polishing and annealing and to send them to AFWL for Auger analysis of the surface contaminants and for tests of multilayer dielectric film adhesion. The samples prepared for the test included the following: three micromachined copper mirrors (one as-received, one ion polished with 5000 $\text{\AA}$ removed, and one which was vacuum annealed at 325°C for one hour after being ion polished, 5000 $\text{\AA}$ removed) and three conventionally polished OFHC copper mirrors with similar surface preparations.

The AFWL Auger analysis of surface contamination showed no significant differences between the micromachined and conventionally polished samples in either the species or amounts of contaminants

on the surface. Both types showed major amounts of Cu, O, and C and minor amounts of Na and K. All of the samples (i.e., as-received, ion polished, and ion polished and annealed) showed about the same amount of oxygen present on the surface. The surface of one of the samples was sputtered in the Auger spectrometer, removing about 600 Å and the oxygen signal disappeared. When the sample was exposed to the atmosphere for several minutes and the spectrometer chamber evacuated again, the oxygen signal returned to its initial level. Finally, the carbon contaminant signal was largest in the as-received sample, smaller in the ion polished sample, and smallest in the ion polished and annealed sample.

A two layer dielectric coating, consisting of a quarter wave (at a wavelength of 10.6 μm) film of ThF_4 and a quarter wave film of ZnSe, was deposited onto each of the six substrates after the Auger analysis was completed. The films were deposited by AFWL personnel, using the following conditions. The substrates were not cleaned prior to film deposition and were at ambient temperature during film deposition. The films were deposited, using electron beam evaporation, at 20 Å/sec for ThF_4 and 25 Å/sec for ZnSe. The pressure during deposition was $2-4 \times 10^{-6}$ Torr. Only one sample showed satisfactory film adherence, the as-received, conventionally polished sample; all others exhibited film adhesion problems.

This is a surprising and puzzling result. Not only did the ion polishing and annealing not reduce the adhesion problem with micro-machined copper substrates, but it apparently resulted in poorer film adherence on the conventionally polished copper substrates with which there is normally no adhesion problem. One should be cautious in drawing conclusions from this test because of the small number of samples involved; however, one can speculate that something about the surface of the conventionally polished copper samples, e.g., a contaminant or damaged layer, aided film adhesion and was removed by ion polishing. In support of this hypothesis, it was noted in Section III-B1 that ion polishing of conventionally polished copper

mirrors resulted in a large decrease in sample absorptance which must have been due to the removal of a contaminant or damaged layer from the sample surface. On the other hand, it is unlikely that a difference in surface contamination caused the difference in adhesion on the conventionally polished and micromachined samples, since the Auger analysis showed no such difference. All of this points out the need for further study of the problem of adhesion of films to micromachined samples, including work on ion polishing and coating in situ which has been shown to produce samples with improved film adherence (ref. 5).

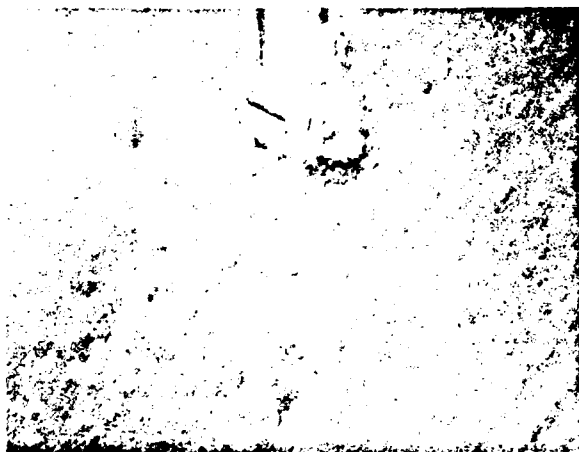
B. Microhardness Versus Annealing Study

It was suggested that a measurement of microhardness of the samples at various stages of surface preparation might be helpful in solving the "coatability" problem of micromachined copper, particularly if the lack of the film adhesion is the result of work hardening of the surface. To this end and also to determine better annealing conditions for copper mirrors, a series of experiments was initiated in which the surface was examined and the microhardness of both micromachined and conventionally polished copper samples was measured after vacuum annealing for 1-1/4 hours at various temperatures. The Knoop hardness was measured, using a Wilson Tukon Model MO hardness tester, as a function of indenter load for loads from 100 gms down to 2 gms. The idea was that the heavier loads would give hardness values that are characteristic of the bulk material while values obtained at the lighter loads would be more representative of the surface. For example, it is estimated that the indenter penetration, for copper with Knoop hardness of 100, is about 4.0 μm for a 100 gm load and 0.89 μm for a 2 gm load; thus, it may be possible to separate surface and bulk annealing effects.

The hardness results are given in table 4. Interference contrast micrographs taken after the various annealings are shown in figures 16 and 17 for micromachined and conventionally polished copper, respectively. Initially, the micromachined copper was softer than the conventionally polished OFHC copper at all loads, and the maximum

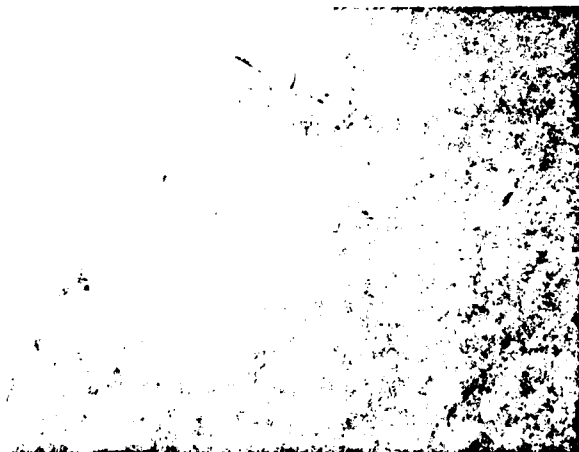


325°C



250°C

20 μ m

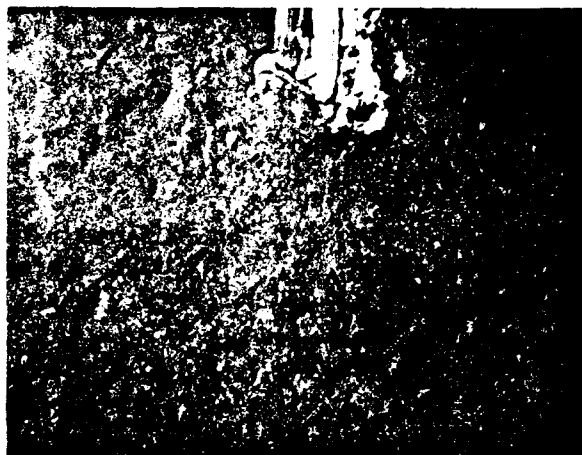


Before Anneal

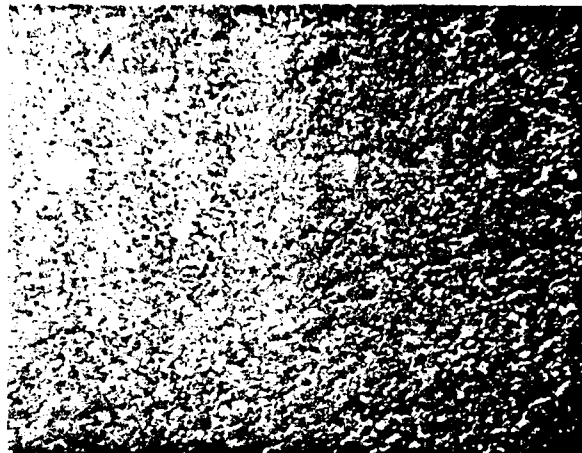
Figure 16. Interference contrast micrographs of micromachined copper after vacuum anneal at various temperatures for 1-1/4 hours.



450°C



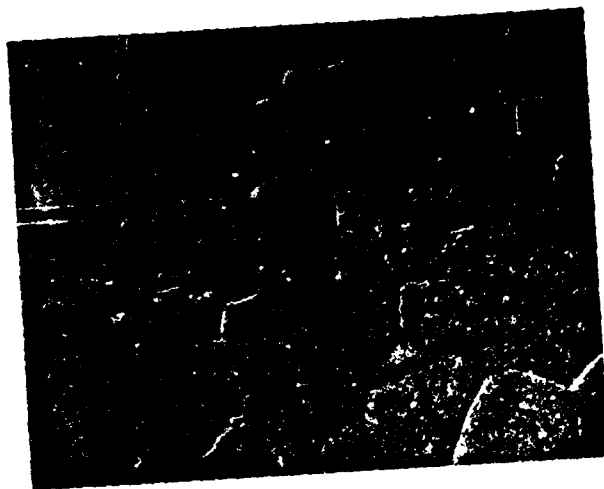
600°C



450°C, Etched

20 μ m

Figure 16. (cont.)

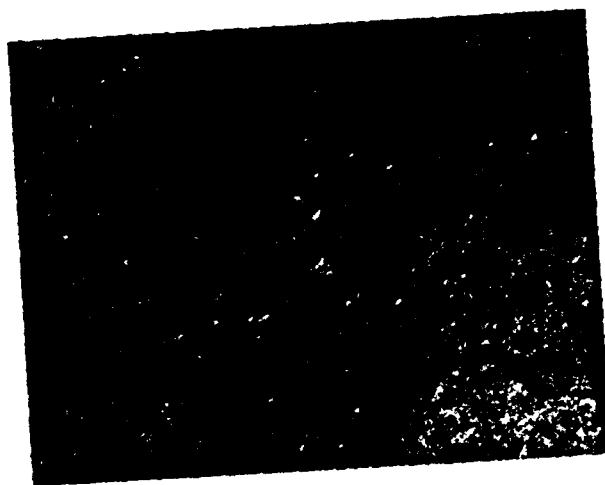


325°C



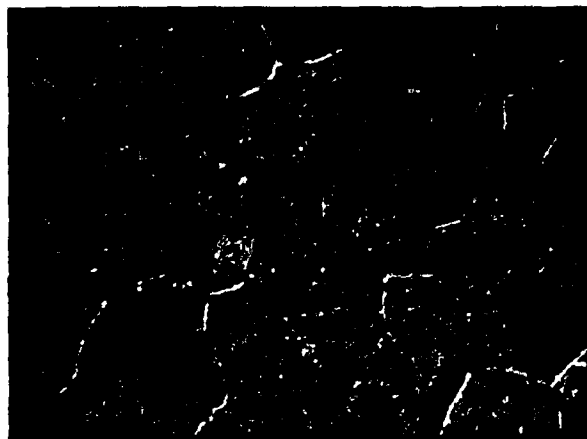
250°C

100 μ m

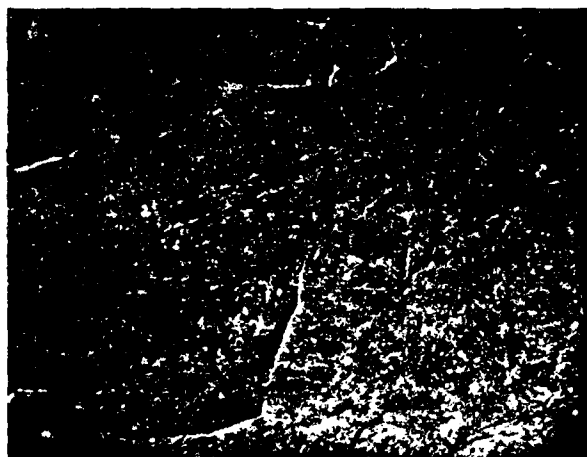


Before Anneal

Figure 17. Interference contrast micrographs of conventionally polished copper after vacuum anneal at various temperatures for 1-1/4 hours.



450°C



600°C

100 μ m



450°C, Etched

Figure 17. (cont.)

TABLE 4

KNOP MICROHARDNESS FOR VARIOUS INDENTER LOADS
AS A FUNCTION OF SAMPLE PREPARATION FOR MICROMACHINED
AND CONVENTIONALLY POLISHED COPPER SAMPLES

Sample Preparation	Knoop Microhardness (kg/mm ²)											
	Micromachined Copper						Conventionally Polished Copper					
	100 gms	50 gms	25 gms	10 gms	5 gms	2 gms	100 gms	50 gms	25 gms	10 gms	5 gms	2 gms
As-received	88.1	92.0	95.3	97.6	102.8	88.2	99.5	105.8	124.0	113.4	107.6	109.8
250°C anneal	86.8	88.5	91.4	89.4	94.5	78.7	105.5	105.5	111.4	121.4	114.1	100.1
325°C anneal	76.3	77.2	81.4	87.6	85.0	77.6	104.6	107.5	111.8	112.7	109.4	105.4
450°C anneal	57.5	60.0	60.8	68.5	63.5	58.7	39.2	39.6	45.8	47.4	50.0	45.8
600°C anneal	48.2	49.8	52.6	56.6	57.1	50.6	35.7	40.2	42.0	43.4	45.3	50.2
Metallographic prep. after 600°C anneal	53.2	48.7	63.7	65.0	65.9	54.0	44.5	48.0	47.7	55.4	52.6	52.7
Metallographic prep. on as-received	57.5	63.2	70.9	74.1	69.0	65.6	105.4	110.6	107.4	112.0	103.8	101.4
- layer	93.2	97.5	106.8	99.8	106.2	99.8						

hardness occurred at an intermediate loading for both types of material. After the first annealing step, 250°C for 1-1/4 hours, the surface of both samples showed enhancement of the crystallite boundaries (Figs. 16 and 17). The micromachined sample was softer at all loads after annealing as compared to before annealing, while the results showed no systematic trend for the conventionally polished sample, i.e., it got harder at some loads and softer at others. Similar results were obtained after the 325°C anneal, i.e., the micromachined sample got even softer, the conventionally polished sample gave mixed results, and both samples showed further delineation of the grain boundaries.

The hardness of the micromachined sample decreased still further after the 450°C anneal while the hardness of the conventionally polished sample fell sharply to a value below that for the micromachined sample. Figures 16 and 17 show that, while there was no dramatic change in the surfaces, some new features appeared on the conventionally polished sample. A ferric nitrate-hydrochloric acid etchant (ref. 10) was used on a portion of both samples to further reveal the grain structure at the surface. Interference contrast micrographs of the surfaces after etching are included in figures 16 and 17, which show the conventionally polished sample to have a much larger grain size ($>100\text{ }\mu\text{m}$) than the micromachined sample ($<10\text{ }\mu\text{m}$). The difference in magnification in the figures should be observed. Finally, the samples were annealed at 600°C and again the micromachined sample became softer while the conventionally polished sample got softer at some loads and harder at others; however, the latter sample was still softer than the former at all loads. The 600°C anneal appeared to result in further, but slight, roughening of the surface of the micromachined sample. It should be noted that the photograph of the conventionally polished sample after 600°C anneal was taken of an area adjacent to the original spot, which was included in the etched area.

Both samples were then subjected to metallographic preparation (consisting of grinding, polishing and etching), photographed, and measured for hardness again. The photographs of the samples (top half of figure 18) show that both now have similar crystallite shapes and sizes. Apparently, there was a fine-grained layer on the surface of the micromachined sample which was removed by the metallographic preparation. The dark spots in the photograph of the micromachined sample are presumed to be oxide particles and indicate that this sample was made from electrolytic tough pitch copper. The photograph of the conventionally polished sample contains no such spots, and it appears that the sample was made from OFHC copper, confirming what was reported to us. The hardness values, also given in table 4, indicate that both samples became harder as a result of the metallographic preparation.

In order to observe the depth and structure of the fine-grained layer at the surface of the micromachined mirrors and to look for a damage layer on the conventionally polished mirrors, samples of both types of material were prepared as follows. A remaining piece of each of the original large specimens supplied by AFWL was electroplated with nickel to preserve the as-received surface condition. These pieces were then cut perpendicularly to the mirror surface and prepared for metallographic examination.

Photographs of these samples are shown in the bottom half of figure 18 and in figure 19. Figure 19a, taken of the micromachined copper sample, shows that there is a fine-grained layer, about 10 mils thick, on the tough pitch copper substrate. The electroplated nickel layer appears as the uniform light grey region on the right hand side of the photograph. In all probability, the fine-grained region is a layer of copper electroplated onto the tough pitch copper substrate, contrary to what we were told. The presence of the sharp layer-substrate interface and the uniformity of the grain structure through the depth of the layer lend support to this being an electroplated copper layer. If the layer were the result of damage caused by the machining operation, one would not expect a sharp interface but rather a gradual change in grain size from the fine-grained structure

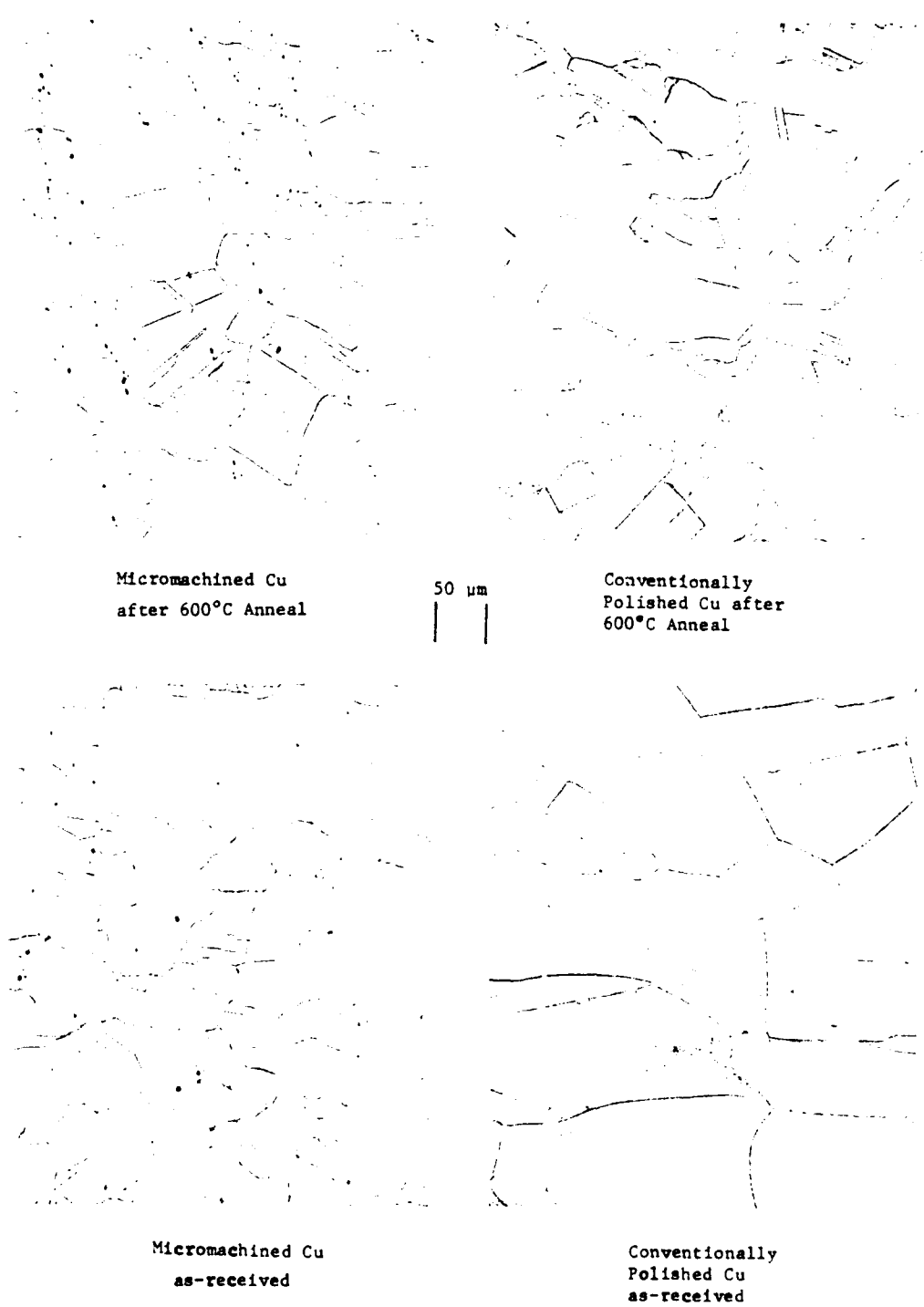
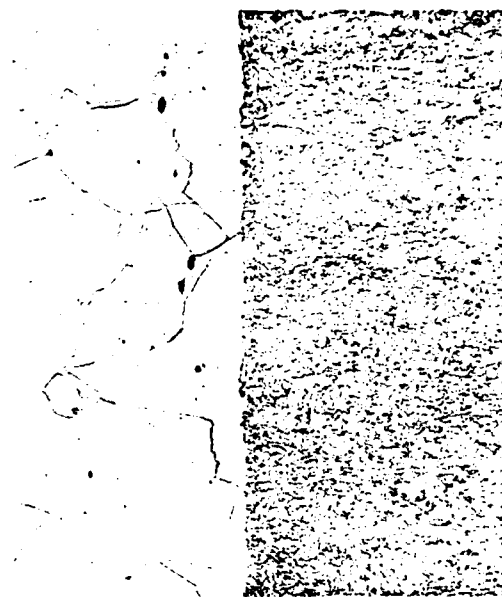


Figure 18. Optical micrographs of copper samples after grinding, polishing, and etching.



a) Micromachined Cu

100 μm



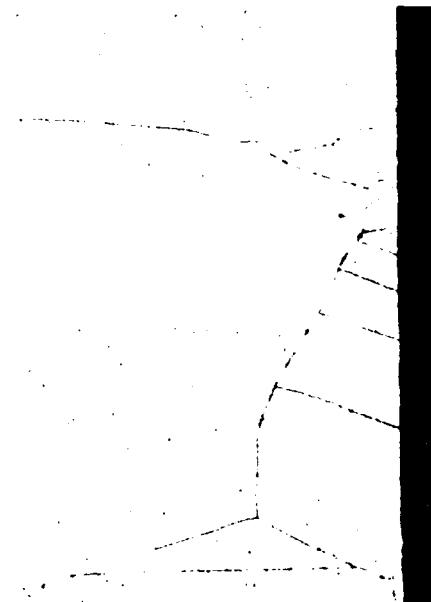
b) Micromachined Cu

20 μm



c) Micromachined Cu

20 μm



d) Conventionally Polished Cu

20 μm

Figure 19. Optical micrographs of copper samples after grinding, polishing and etching perpendicular to the mirror surface.

at the surface to the coarse grains of the bulk. Figures 19b and 19c show photographs at higher magnification of the substrate-copper layer interface and the copper layer-nickel layer interface, respectively. Figure 19d is a photograph of the interface between the mirror surface of the conventionally polished sample and the electroplated nickel; the dark strip on the right hand side of the photograph is the result of poor adherence of the nickel layer to the copper sample. It can be observed that there is no evidence in these photographs of damage to the surfaces of the samples or at the electroplated copper layer--substrate interface.

The two pictures in the bottom half of figure 18 show the grain structure of the interior of the samples before annealing and should be compared with the photographs after annealing shown in the upper half of this figure. It is seen that the micro-machined copper substrate, excluding the fine-grained layer, exhibited similar grain structure and size before and after annealing, while the conventionally polished copper sample showed a significantly larger grain size before annealing than after annealing.

Microhardness measurements taken on the as-received (unannealed) samples following the metallographic preparation are also included in table 4. Hardness values are given for both the substrate and fine-grained layer of the micromachined sample. It is seen that the fine-grained layer was much harder than the substrate material and slightly harder than the original micromachined sample (first line of table 4). Perhaps this latter difference arises because the original values were obtained on the mirror surface of the layer, which was micromachined, and the last values were measured on the layer after it was subjected to the metallographic preparation, i.e., grinding, polishing, and etching. It would thus appear that grinding and polishing damage (harden) a surface more than micromachining. For the conventionally polished sample, the hardness values were higher for some of the loads after metallographic preparation, as compared to the original values, and were lower for other loads, but they were much higher than the values obtained for the interior of the substrate of the micromachined sample.

It was noted when discussing figure 18 that the grain size of the conventionally polished sample before annealing was considerably larger than that of the micromachined substrate, and thus, one would expect the conventionally polished sample to be softer. Since the conventionally polished sample was actually harder, it must have been highly strained before annealing, and careful examination of figure 18 shows this to be the case. After the 450°C anneal, the conventionally polished sample softened dramatically. At this stage the grain size was not examined; however, following the 600°C anneal, the sample was etched and photographed (upper left photograph of figure 18). It is seen that the grain size decreased significantly during annealing. This decrease in grain size with annealing, contrary to the normal grain growth with annealing, is observed when annealing highly strained samples, which apparently was the case with the conventionally polished samples (ref. 11).

In conclusion, it was found during the course of the hardness versus annealing study that there was a fine-grained layer (in all probability it was electrodeposited) on the micromachined copper samples and that this layer was responsible for the different crystallite structure noted in Section III-A. Furthermore, this layer did not blister or peel during vacuum annealing up to 600°C. Initially, the hardness of the conventionally polished sample exceeded that of the micromachined sample, while after the several annealing steps, the micromachined sample hardness was greater than that of the conventionally polished sample. The hardness values for both samples decreased with anneal; the micromachined sample hardness decreased systematically while the decrease for the conventionally polished sample occurred principally in a large change upon annealing at 450°C. Enhancement of the crystallites on the surfaces of both types of samples was seen after annealing at only 250°C for 1-1/4 hours. Finally, the poor film adherence to micromachined samples may be associated with the fine-grained structure of the deposited layer, or alternatively, the good adhesion on the conventionally polished substrates may result from the highly strained (hardened) state of the surface.

C. Effects of Ultrasonic Cleaning

Both the micromachined and conventionally polished copper samples used in this study exhibited small defects which appeared to be pits on the surface. These defects occurred in widely varying concentrations even over the same sample (see figure 3, for example). It was reported that ultrasonic cleaning lowers laser damage thresholds, presumably because of surface damage produced in the ultrasonic cleaning process (ref. 12). Since the present samples were cut from larger samples and subjected to ultrasonic cleaning, it appeared judicious to investigate the possibility that the defects were caused by the ultrasonic cleaning. The two 1-1/2 in. diam micromachined copper samples that were not subjected to ultrasonic cleaning by us were examined and also found to contain the types of defect described. Subsequently, we were told that in all probability these samples were ultrasonically cleaned after the micromachining operation. The two large conventionally polished copper samples and the two large molybdenum samples, which were thought never to have been subjected to ultrasonic cleaning, were found to be free of the type of defect described. One of these copper samples was then ultrasonically cleaned in methyl alcohol for 20 minutes in a small ultrasonic cleaner having a maximum acoustic power of about 10 watts. Examination of the surface with the interference contrast microscope gave results similar to those shown in figure 3, i.e., pitting of the surface in varying degrees over the sample. There was no evidence of damage on the surface of a molybdenum sample that was subjected to similar ultrasonic cleaning. Thus, it is concluded that ultrasonic cleaning, at this power level and duration, does introduce surface damage in both micromachined and conventionally polished copper samples but does not visibly damage molybdenum samples.

As mentioned in Section III, the absorptances of both the micromachined and conventionally polished copper samples, measured by calorimetry after cutting from the larger samples and cleaning in the ultrasonic cleaner, were significantly higher than those values determined

by reflectivity at AFWL, while good agreement was found for the molybdenum samples. This suggested that the higher absorptance values measured here for the copper samples may be related to damage from ultrasonic cleaning. In order to investigate this possibility, the absorptance of a micromachined copper sample was measured and its surface examined using the interference contrast microscope at various stages of ultrasonic cleaning. The results are listed below and shown in figure 20.

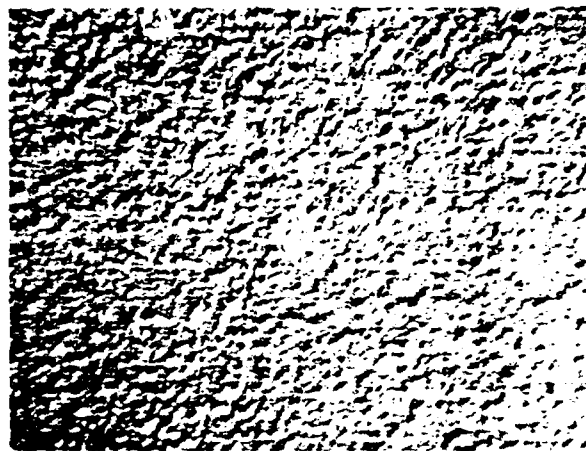
absorptance = 0.834%, starting value (compare with 0.85% measured at AFWL by reflectivity).

0.809%, after ultrasonic cleaning (30 minutes in methyl alcohol).

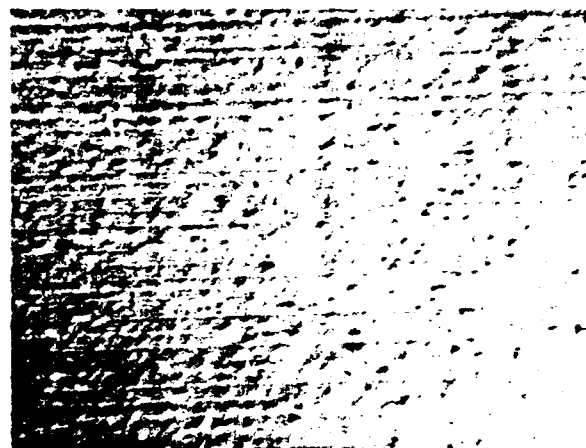
0.808%, after 2nd ultrasonic cleaning (30 minutes in trichloroethylene, 60 minutes total).

Examination of figure 20 shows that ultrasonic cleaning of micromachined copper for 30 minutes in methyl alcohol does indeed introduce considerable visible surface damage; however, the absorptance at 10.6 μm actually decreased slightly. The sample was then subjected to further ultrasonic cleaning, this time using trichloroethylene to see if a different solvent had any effect. After the second ultrasonic cleaning step, 60 minutes total, the surface was heavily damaged, as seen in figure 20 and by observation of the increase in scatter of the He-Ne alignment laser, but the absorptance did not increase.

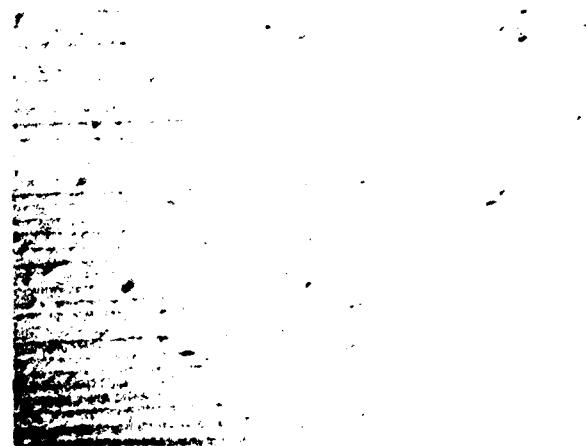
We conclude that ultrasonic cleaning of copper surfaces, using various organic solvents, does cause visible damage (pitting) and increased scattering of light but does not cause any increase in the absorptance at 10.6 μm . The discrepancy in the absorptance measurements for copper, mentioned previously, and which incidently was not seen in the initial value in the above data, must have some cause other than damage due to ultrasonic cleaning. A further conclusion, also discussed in Section III-A4, is that the absorptance at a wavelength of 10.6 μm does not appear to be a function of the surface finish, at least for the types of surface roughness shown in the figures.



After Ultrasonic
Cleaning for
60 Minutes



After Ultrasonic
Cleaning for
30 Minutes



Before Ultrasonic
Cleaning

50 μ

Figure 20. Interference contrast micrographs of a micromachined copper sample after various stages of ultrasonic cleaning.

V. CONCLUSIONS

The following major results were obtained during the course of this study.

- The combination of ion polishing and vacuum annealing afforded a small decrease, 5 to 10%, in the absorptance at 10.6 μm for micromachined copper and molybdenum samples but resulted in a large decrease, 40 to 50%, in the absorptance of conventionally polished copper.
- The absorptance of the as-received micromachined copper mirrors was very low, leaving little room for improvement.
- Ion polishing and annealing of the conventionally polished copper reduced the absorptance to a value as low as that for micromachined mirrors.
- Annealing both types of copper mirrors at 325°C for 1-1/4 hours yielded a decrease in absorptance after ion polishing but at the expense of grain boundary enhancement.
- For molybdenum mirrors, vacuum annealing at 800°C for 1 hour, with no ion polishing, resulted in a decrease in the absorptance of about 10% with no evidence of surface roughening.
- Ion polishing proved beneficial in removing surface defects, such as machining marks, scratches, and oxide layers; however, for large amounts of material removed, differential sputtering of the various crystallites led to grain boundary delineation and surface roughening, even under the conditions of relatively low energy ions incident at glancing angle.

- There is an optimum amount of material to be removed by ion polishing which results in both maximum removal of surface defects and minimum roughening of the surface. Removal of this optimum amount does not necessarily yield the minimum sample absorptance.
- The optimum amount to be removed by ion polishing depends upon the mirror material and its previous preparation. The values found are:
 - Micromachined copper, 2500 to 5000 Å,
 - Conventionally polished copper, 5000 to 7000 Å,
 - Molybdenum, ≤ 1500 Å.
- In order to minimize surface roughening due to differential crystallite sputtering, the ion polishing should be completed before annealing the sample.
- Ion polishing of conventionally polished copper mirrors revealed, and subsequently removed, dielectric polishing grit embedded in the sample surface. The removal of such grit is essential for the production of mirrors with a high laser damage threshold.
- Ion polishing of molybdenum in which more than 1500 Å was removed, resulted in pitting of the surface and is attributed to flaws in the original material. Again, the presence of such defects near the surface can significantly lower the laser damage threshold.
- A fine-grained copper layer, in all probability electro-deposited, was found on the surface of the micromachined samples. This layer did not peel or blister with vacuum annealing up to 600°C.
- Combinations of ion polishing and vacuum annealing were found to reduce the level of contaminants, most notably carbon, on the surfaces of micromachined and conventionally polished copper. No significant differences between the surface contamination on the micromachined and conventionally polished samples were found.

- Not only did ion polishing and vacuum annealing fail to improve the adherence of a two-layer dielectric film (subsequently deposited at AFWL) on micromachined copper, but resulted in decreased adherence on similarly-prepared, conventionally polished copper.
- The Knoop microhardness of the conventionally polished copper was initially higher than that of the micromachined copper, but after annealing both at 450°C, the opposite was true. The micromachined sample became progressively softer with annealing at 250°, 325°, 450°, and 600°C, while the conventionally polished sample became softer in one large step, after the 450°C anneal.
- Ultrasonic cleaning in various organic solvents caused visible surface damage on copper mirrors, but no such damage was observed on molybdenum samples. The damage to the copper mirrors did not result in an increase in absorptance at 10.6 μm .
- No correlation between surface roughness and absorptance at 10.6 μm was found, at least for the types of roughness caused by ion polishing or ultrasonic cleaning.

VI. RECOMMENDATIONS FOR FUTURE STUDY

As a result of this study it is suggested that the following areas be further investigated as potential methods for producing improved high power laser mirrors with lower absorptance and scatter and higher damage threshold.

- Methods for minimizing differential sputtering of the crystallites during ion polishing of polycrystalline material should be investigated. These include: removing only the disordered, surface-damage layer and then annealing; ion polishing at a reduced sample temperature to prevent self-annealing of the surface during polishing; and ion polishing using a continually varying angle of incidence of the ion beam to average the angle-of-incidence and crystallite orientation effects.
- A further annealing study of copper samples should be carried out, which includes annealing without ion polishing, in an attempt to achieve a reduction in sample absorptance without an increase in surface roughness due to grain growth or thermal etch.
- Methods for improving multilayer dielectric film adhesion to micromachined copper substrates should be investigated. An obvious approach consists of performing the ion polishing, vacuum annealing, and depositing the overcoating films in situ. Another approach to this problem involves identification of the factors which aid film adhesion on conventionally polished copper but are removed during ion polishing. If the cause of the film adhesion could be identified, perhaps one could apply this information to improve film adherence on the micromachined samples.

- Finally, sample mirrors prepared with various combinations of ion polishing and vacuum annealing should be subjected to laser damage testing to determine whether or not an increase in laser damage threshold occurs as a result of the decreased absorptance and removal of surface defects and contaminants.

PERMANENT RECORD BOOK ENTRIES

Book #206924 - Entire Book

Book #207469 - Entire Book

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