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ADHESION BETWEEN CVD DIAMOND FILMS AND TUNGSTEN

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Abstract

Adhesion between diamond films synthesized by a CVD method and tungsten has been investigated by scratch and pull testing methods. Diamond films have been deposited at temperatures from 1173 to 1323 K with a growth rate ranging from 0.2 to 0.45 μm/hour. The films are highly crystalline and are dominated by (100) faces at low temperatures, changing to (111) at higher temperatures. Grain size and residual stress in the films increases with increasing deposition temperature. X-ray diffraction shows the expected diamond diffraction peaks plus peaks attributed to WC and W_2C. Raman spectroscopy shows a sharp diamond band for all of the films, with a small broad peak attributed to amorphous carbon. There is no distinct correlation between diamond/amorphous carbon intensity with deposition temperature. Scratch adhesion testing shows the expected failure mode for brittle coatings, but can not be quantified because of severe degradation of the diamond stylus tip. Sebastion pull testing shows that the failure mode of the films correlates with deposition temperature, but specific adhesion strength values do not. Efforts are continuing to correlate adhesion strength with deposition and structural parameters of the diamond films.

INTRODUCTION

Chemically vapor deposited polycrystalline diamond films are potential candidates as wear resistant coatings on cutting tools, bearings and other high wear surfaces. A prerequisite in this regard is good adhesion between the diamond film and the substrate, because any protective coating is useful only as long as it adheres to the substrate. Despite its importance, the adhesion of diamond films to various substrates has received only limited interest in the past (1-5). An understanding of the adhesion of diamond films to substrate materials and how it can be improved is of considerable importance. This paper deals with the measurement of adhesion of CVD diamond films and its correlations with substrate temperature, growth rate and film characteristics. Such correlations are necessary to arrive at some general guidelines for synthesizing good quality diamond films at high growth rates and with good adhesion.

EXPERIMENTAL

Diamond films were deposited on a 22 mm diameter area on 25 x 25 x 1.6 mm polycrystalline tungsten substrates from CH_4-H_2 gas mixtures by a hot filament assisted CVD technique in a bell jar system, using tungsten ribbon filaments (0.762 mm wide by 0.0762 mm thick). The films were prepared at 1173, 1223, 1273 and 1323

K. All other deposition parameters were kept constant: filament temperature = 2273 K, system pressure 30 torr, gas flow rate = 100 sccm, CH_4 content of the input gas = 0.5 % by volume, distance between the filament and the substrate = 5 mm. Prior to deposition the substrates were polished down to 5 μm size alumina powder, ultrasonically cleaned with methanol and seeded by scratching the tungsten with 43 μm diamond powder. Typical film thickness ranged from 5 to 10 μm.

The films were characterized with regard to morphology by scanning electron microscopy (SEM), structure by Raman spectroscopy, crystallinity and residual stress by x-ray diffraction and adhesion by both scratch and tensile pull testing. Raman spectra were taken from a 2 mm by 0.1 mm area of the sample using both the 514.5 nm and the 457.9 nm lines of an argon ion laser with a monochromator resolution of 6 cm^{-1}. Scratch adhesion testing was performed using a CSEM Revetest acoustic emission scratch tester with progressively increasing load at a loading rate of 100 N/min and a table speed of 10 mm/min. The tip was a Rockwell C diamond with a 120° cone angle and a 200 μm tip radius. The tensile pull adhesion testing was performed with a Quad Group Sebastion tester using 1/8" diameter studs. The epoxy-bonded studs were cured at 150°C for 1 hour after mounting on the samples.

RESULTS AND DISCUSSION

Growth Rate

The average growth rates in terms of film thickness per unit time were measured from the knowledge of the weight gained by the samples during the deposition period (22.25 hours), the diameter of the deposited film area (2.22 cm) and assuming a film density equal to bulk diamond (3.52 g/cm^3). The dependence of film growth rate on temperature is shown in Figure 1. The growth rate reaches a maximum at about 1223 K. The apparent activation energy up to 1223 K is 95 kJ/mole. The decline in the growth rate beyond 1223 K may be attributed to the increased thermal desorption of hydrogen and carbon-containing species at the growth surface.

Morphology

Typical morphologies of diamond films synthesized at different substrate temperatures are shown in Figure 2. At 1173 K the film is dominated by (100) surfaces and the crystallites are rather small. At 1223 K, the predominant morphology is still cubic, however, the individual grains are relatively larger. At 1273 K, (111) surfaces begin to appear. At 1323 K the film is dominated by octahedral faces. Cubo-octohedra can also be seen.

Structure

X-ray diffraction measurements indicated the presence of all three diamond peaks, (111), (220) and (311) in the 2θ range scanned. An internal standard was used to measure the precise peak positions. No shift in the positions of the peaks was observed. Signals from non-diamond carbon phases were not observed. X-ray diffraction, however, did indicate the presence of WC and W_2C.

Raman spectra of the diamond films are presented in Figure 3. The peak intensities are normalized with respect to the broad band. All samples show a good sharp diamond band at 1333 cm^{-1}. For all of the samples, this band is broader and shifted to higher wavenumber, relative to a gem quality natural diamond standard. The broadening is most likely a result of non-uniform strain in the deposited diamond films. The shift in the peak is probably due to a shortening of the bond length, relative to the diamond standard, as a result of compressive stresses in the film. The broad band near 1550 cm^{-1} represents an amorphous type carbon. These effects are in agreement with the x-ray diffraction results presented below. The ratio of the intensity of the diamond band relative to the amorphous carbon band varies with the sample and substrate temperature and is summarized in Table 1 for two sets of samples. It can be seen that there is a large difference from sample to sample that overshadows the differences seen as a function of temperature. This difference between repeat samples is largest at each of the temperature extremes; much closer values are obtained for the intermediate temperatures.

Residual Stress

Diamond films produced by the CVD process on any substrate are under strain due to a variety of reasons. The strain is either uniform or non-uniform. In terms of x-ray diffraction patterns, each type of strain has a distinct effect. Uniform strain causes a shift in peak positions. Since no shift was observed, the strain in the films is not uniform. Non-uniform strain leads to peak broadening. Broadening is also caused by fine particles in the film (< 0.1 μm) and the instrument itself. In all films, particles are larger than 0.1 μm. So the measured peak widths have no contribution from particle size effects. Instrument broadening effects were assumed to be negligible. Therefore, measured peak widths (full width at half maximum) are attributed to non-uniform strain alone. Non-uniform strain was calculated from the peak width and position data utilizing a standard procedure (6). Since the films had different thicknesses, the measured strain values were normalized with respect to thickness. The data is presented in Figure 4 as a function of substrate temperature. The strain in the films increases with substrate temperature. The higher thermal expansion of tungsten relative to diamond causes the films to be in compression once the samples are cooled down to room temperature.

Adhesion

Scratch adhesion testing produced clear acoustic emission detection of the failure of the diamond films. The failure mode was very similar to that observed previously for diamond films on silicon (4) - initial cracking of the film followed by large scale delamination of the film around the scratch as the critical normal load is reached. However, reproducible and quantifiable critical normal loads were not able to be obtained because of extensive damage to the Rockwell C diamond stylus. The previous successful results for diamond on silicon were obtained with thin diamond films (2.5 μm) consisting of a very small grain size (< 100 nm). The present films are much thicker and have a much larger grain size, with sharp faceted features. The morphology of these films tends to grind the Rockwell C diamond stylus flat very quickly. This grinding process changes the tip radius and size constantly during the scratch testing process, making it difficult to quantify critical normal loads (7). Figure 5 shows SEM micrographs for an undamaged Rockwell C diamond stylus tip and a tip which has been used for only 3 scratch-testing passes across a single diamond film surface. Figure 5 also shows a tip which has been used for 50 scratch-testing passes on a variety of the diamond film surfaces. This continual grinding process make scratch testing a poor tool for adhesion testing of these diamond film surfaces.

An alternative Sebastion pull testing technique was also used to test the adhesion of the diamond films. This testing showed three distinct failure modes of the film. The first failure mode resulted in a clean pull of the film from the epoxied-stud surface area, leaving a circular area of the substrate free of the diamond film. This type of failure mode was observed most often for the films deposited at the lower temperatures. As the temperature was increased, the amount of film pulled free of the sample decreased, leaving substrate areas which had only partial removal of the film. At the highest temperatures, a second failure mode was typically observed, which resulted in only very small spots of the film being removed. This range of film removal is illustrated in the photographs in Figure 6. In Figure 6 (a), the circular dark area in the center shows where the diamond film has been completely removed from the substrate. The light regions surrounding the center zone show areas where the diamond film has delaminated from the substrate, but has not been removed. The other panels of Figure 6 show the decreasing areas of film removal as the deposition temperature is increased. In Figure 6 (d), it can be seen that only very small, limited portions of the film have been removed from the substrate. A small number of the samples exhibited a third failure mode which resulted in total delamination of almost the whole diamond-film coated area from a single adhesion pull test. The samples exhibiting this total delamination did not share a common deposition temperature, film thickness or diamond/amorphous carbon Raman intensity, suggesting that poor surface preparation may be the problem with the few samples. The measured film adhesion ranges from 260 psi to > 10,220 psi and does not appear to correlate with deposition temperature, film thickness (growth rate), or the diamond/amorphous carbon Raman intensity. In fact, the variation in the adhesion values from one location to another on a single sample far outweighs the differences observed from sample to sample. This adhesion data is summarized in Table 2. Efforts are continuing to find reliable ways to measure the adhesion of the diamond films and to correlate the adhesion with the deposition or structural parameters of the films.

SUMMARY

Diamond films have been deposited on tungsten at substrate temperatures of 1173, 1223, 1273 and 1323 K. The growth rate was lowest at each of the temperature extremes, and highest at 1223 K. The growth rate ranged from 0.2 to 0.45 μm/hour, resulting in film thicknesses of 5 to 10 μm after 22.25 hours of deposition.

The apparent activation energy for the film deposition is 95 kJ/mole. The films are dominated by (100) surfaces at low temperatures and change to (111) surfaces as the temperature increases. The grain size also increases as the temperature increases. The films are very crystalline in appearance, with typically sharp cubic and octahedral facets common. X-ray diffraction shows all expected diamond peaks with some additional peaks attributed to WC and W_2C. Raman spectroscopy shows a sharp diamond band for all of the spectra and a smaller, broad band due to amorphous carbon. The ratio of the diamond to amorphous carbon intensities as measured by Raman spectroscopy vary from sample to sample, but do not appear to be a strong function of the deposition temperature. The residual stress of the diamond films has been measured by the broadening of the x-ray diffraction lines. The stress in the films increases as the deposition temperature increases, as a result of the differences in thermal expansion between the diamond films and the tungsten substrates. Scratch adhesion testing displays the failure mode expected for brittle coatings, but quantitative adhesion values can not be obtained because of excessive wear of the diamond stylus tip by the highly faceted film surfaces. Sebastion adhesion testing shows that the failure mode of the films varies with the deposition temperature, with removal of the film over the entire surface area of the stud occurring only at low temperatures. As the temperature in increased, the amount of film removal over the surface area of the stud decreases, until only very small portions of the film are removed at the highest deposition temperature. However, the variation in adhesion strength from point-to-point on individual samples is as large as the variations that could be attributed to differences in deposition temperature. No strong correlations of adhesion strength with deposition temperature, film thickness, residual stress, or diamond/amorphous carbon intensity have been observed. Efforts are continuing to find reliable ways to measure the adhesion of the diamond films and to correlate the adhesion with the deposition or structural parameters of the films.

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TABLE 1

Ratio of the intensity in the Raman diamond band relative to the intensity in the amorphous carbon band as a function of deposition temperature, using the 457.9 nm laser line. Values are reported for two different sets of samples.

Sample	Temperature (K)	Diamond/Amorphous C
1	1173	13.5
2	1173	5.1
3	1223	3.6
4	1223	4.3
5	1273	8.2
6	1273	5.8
7	1323	18.4
8	1323	2.2

TABLE 2

Adhesion testing values as a function of deposition temperature. Values are reported for two different sets of samples. The multiple adhesion values listed for each row of the table result from multiple pull tests on the same sample, in the order that the repetitive tests were performed.

Sample	Temperature (K)	Adhesion Values (psi)			
1	1173	delaminated			
2	1173	450	6590	680	
3	1223	1620	5040		
4	1223	260	10080	850	
5	1273	6770	1830	>10220	
6	1273	1210	8010		
7	1323	9260	9720	4560	6660
8	1323	8990	10230	delaminated	

FIGURE CAPTIONS

Figure 1: Arrhenium plot of the rate data.

Figure 2: Typical SEM micrographs of diamond films prepared at (a) 1173 K, (b) 1123 K, (c) 1273 K, and (d) 1323 K.

Figure 3: Raman spectra of diamond films with intensity of each spectrum normalized to the broad band peak near 1550 cm^{-1}.

Figure 4: Strain in the films versus substrate temperature.

Figure 5: SEM micrographs of Rockwell C diamond stylus tips used for scratch adhesion testing after (a) no scratches, (b) 3 scratches on a single film surface, and (c) 50 scratches on a variety of diamond film surfaces.

Figure 6: Photographs of typical Sebastion pull-testing scars from films deposited at (a) 1173 K, (b) 1223 K, (c) 1273 K, and (d) 1323 K.

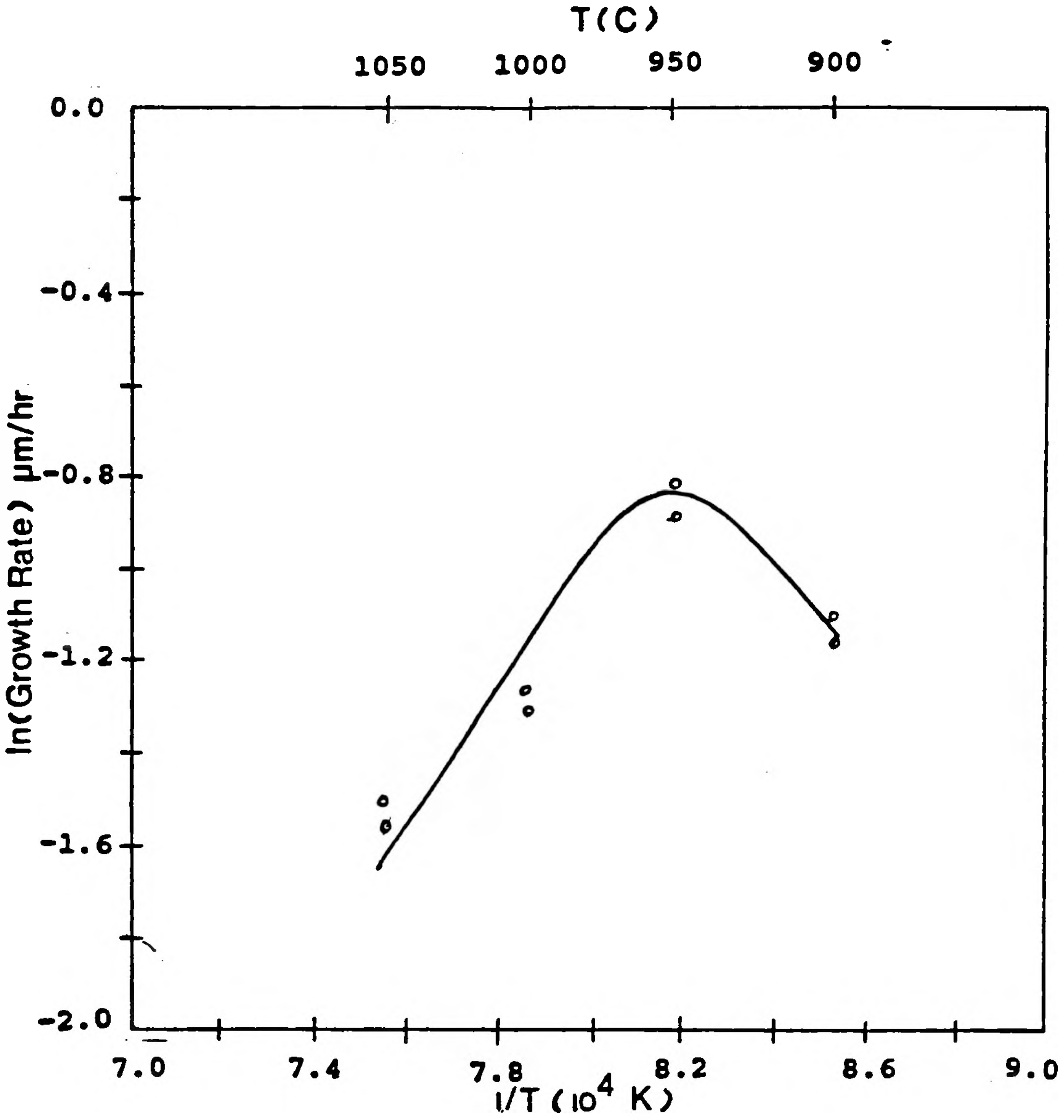

T(C)
1050
1000
950
900
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
ln(Growth Rate) µm/hr
7.0
7.4
7.8
8.2
8.6
9.0
1/T (10⁴ K)

Fig 1

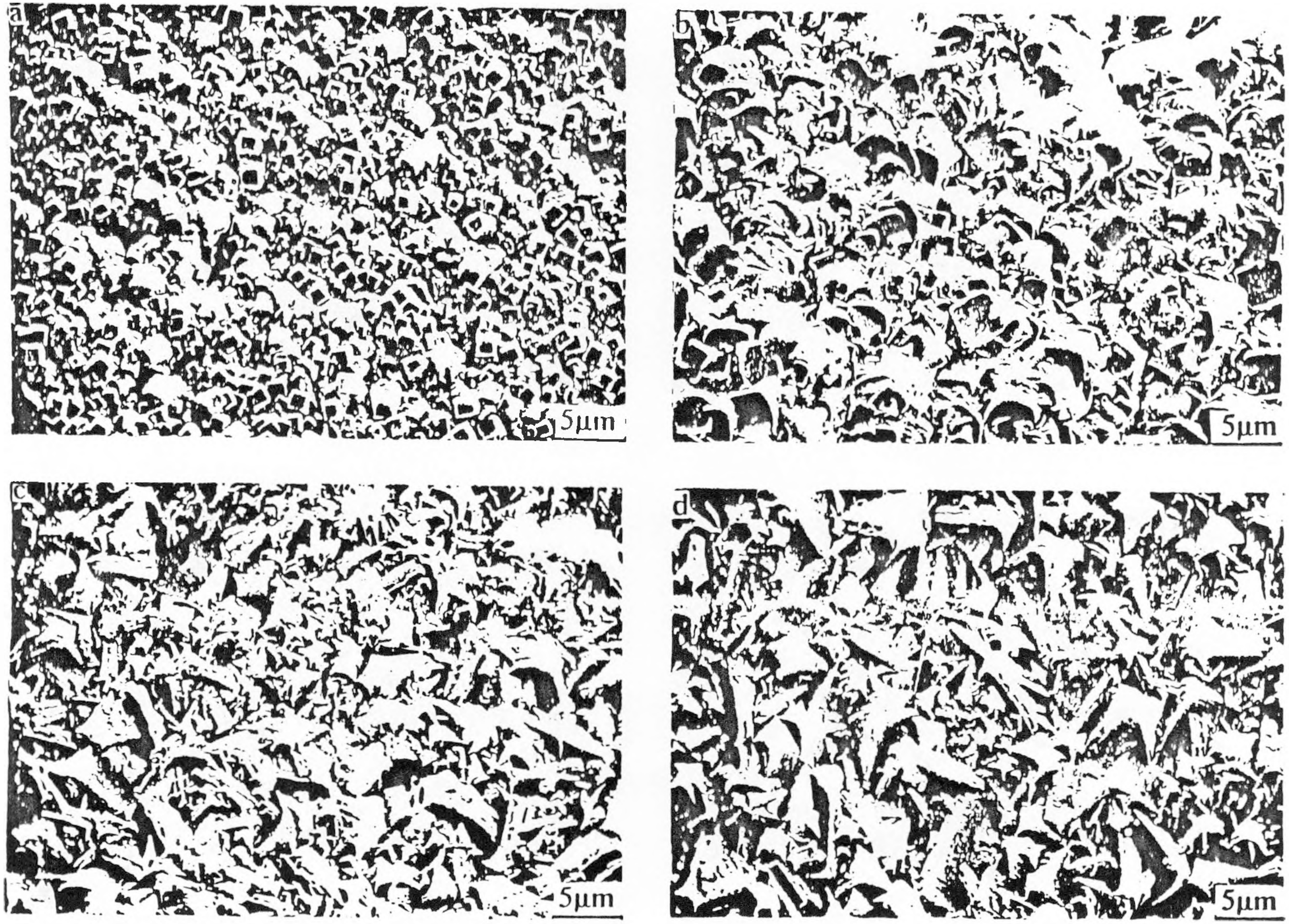


Fig. 2

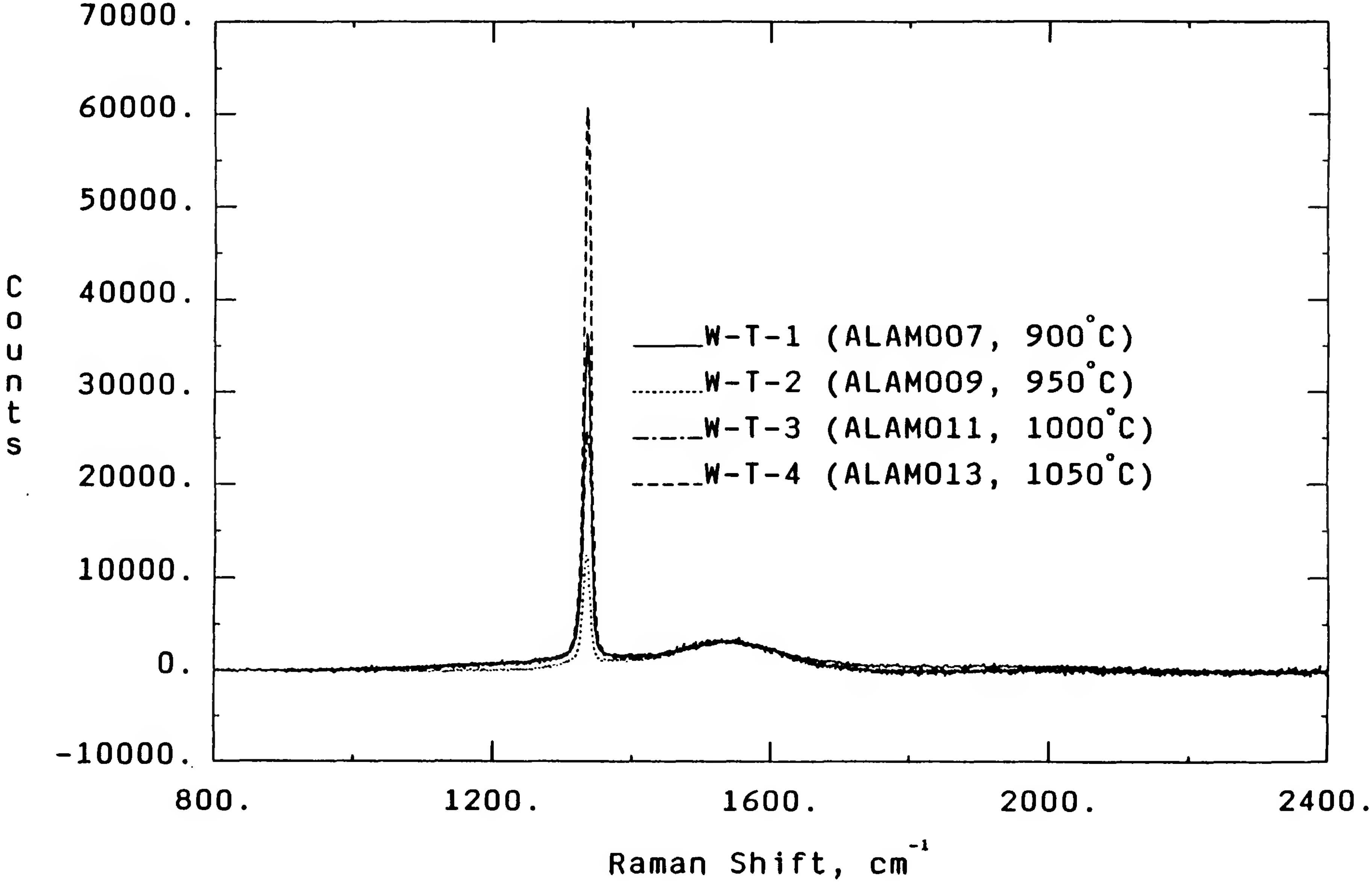

70000.
60000.
50000.
40000.
30000.
20000.
10000.
0.
-10000.
Counts
800.
1200.
1600.
2000.
2400.
Raman Shift, cm⁻¹
W-T-1 (ALAM007, 900°C)
W-T-2 (ALAM009, 950°C)
W-T-3 (ALAM011, 1000°C)
W-T-4 (ALAM013, 1050°C)

Fig. 3

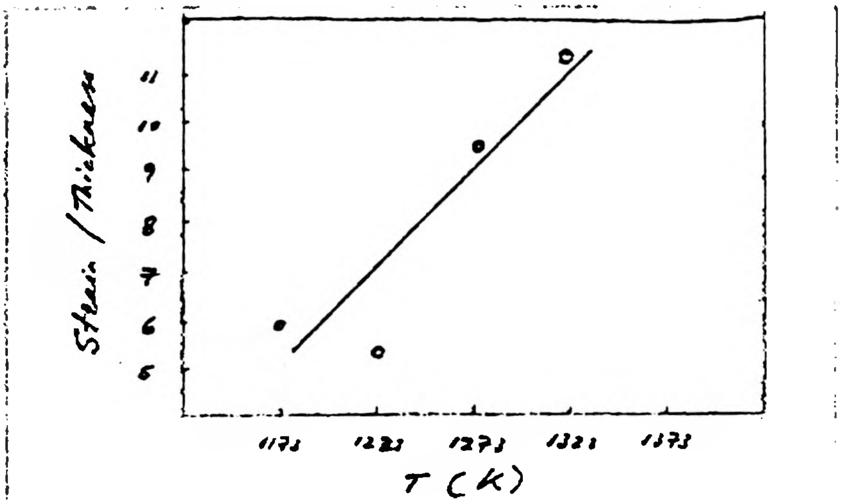
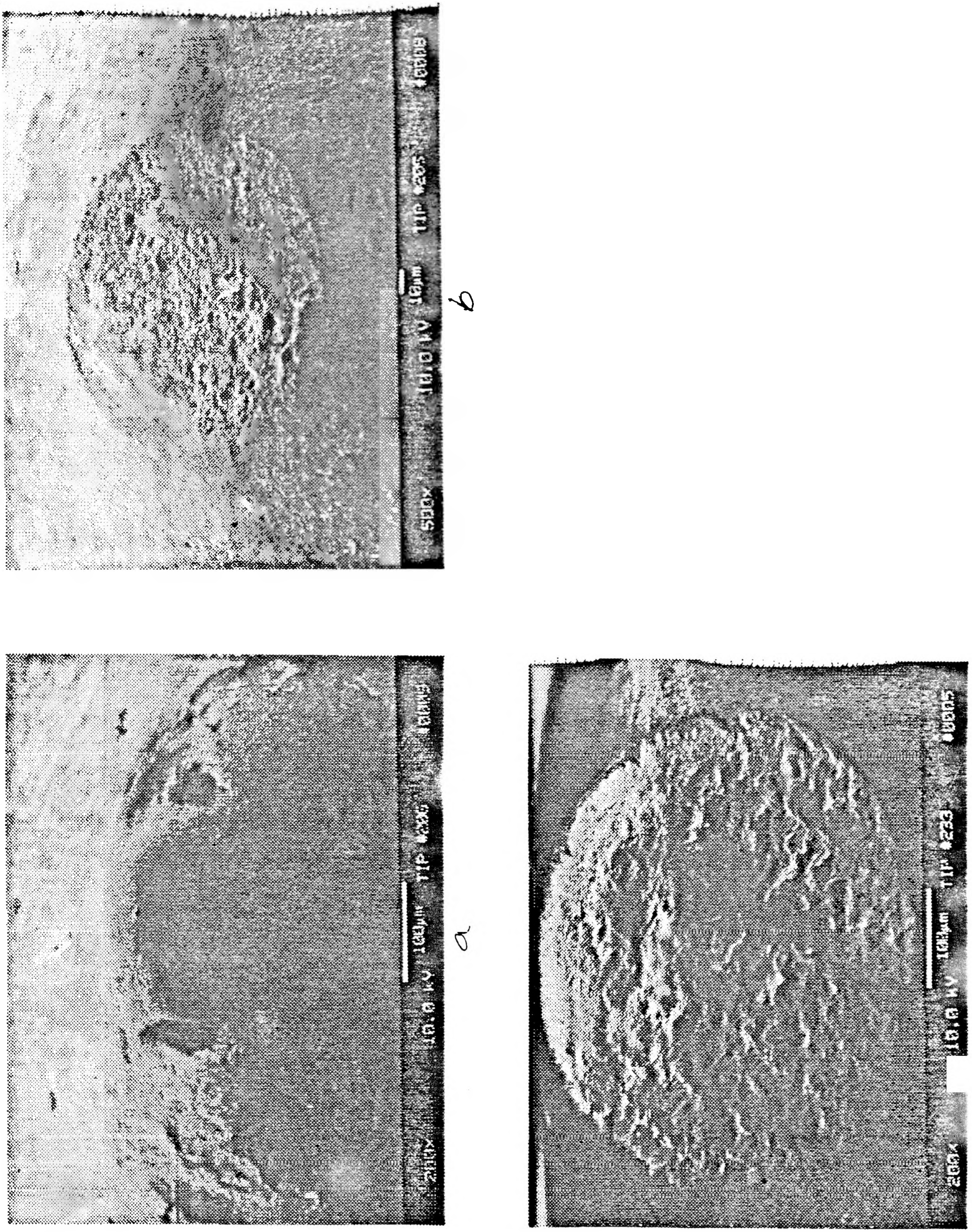


Fig. 4


500x 10.0 kV 10μm TIP #205 #0008
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200x 10.0 kV 100μm TIP #233 #0005

a

b

c

Fig. 5

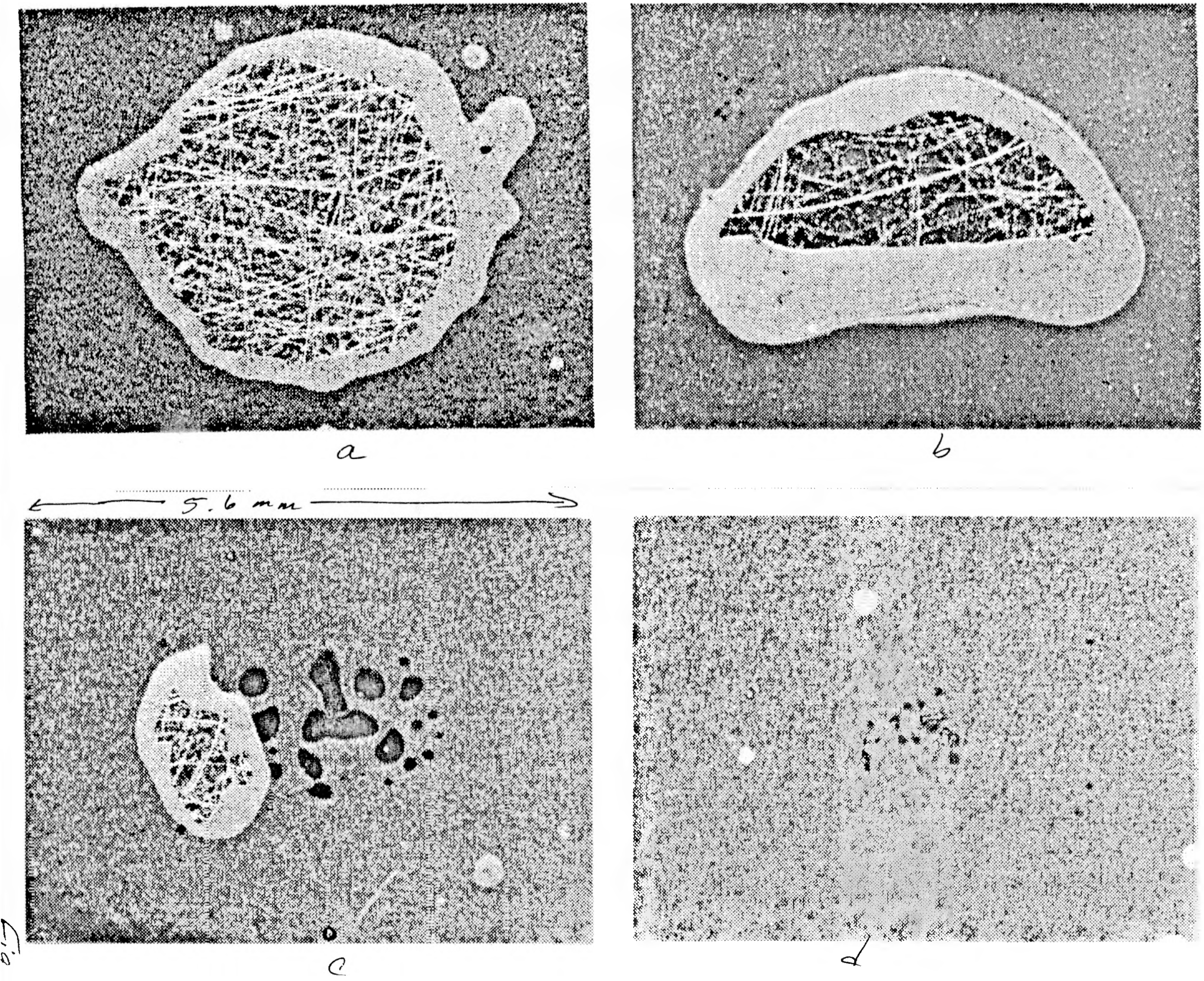

Fig 1