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TITLE: Characterization of Aluminum/Aluminum Nitride Coatings Sputter Deposited Using the Pulsed-Gas Process

AUTHOR(S): R. W. Springer and C. D. Hosford

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Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

CHARACTERIZATION OF ALUMINUM-ALUMINUM NITRIDE COATINGS SPUTTER DEPOSITED USING THE PULSED GAS PROCESS

R. W. Springer and C. D. Hosford

Los Alamos National Laboratory

Abstract

A DC triode magnetron has been used to produce freestanding Al/Al+AlN lamellar foils by sputter deposition. The 5-μm-thick foils produced on both flat substrates as well as curved substrates exhibited good specularity as well as excellent mechanical properties.

The pulse spacing was varied from none to 160-nm spacing. The yield strength of [illegible] material was found to obey the Hall-Petch relation

σ_{ys} [illegible]

where σ_{ys} is in MPa. Auger Electron Spectroscopy and Secondary Ion Mass Spectroscopy indicate that the large flow stress of [illegible] MPa must be due to grain refinement of the extended source and not an impurity effect. The result is that limitations of masking found in uniaxial flux sources for curved surfaces can be removed allowing the high quality coating of more general shapes.

Introduction

The opportunity to synthesize new materials and produce composites using vapor and sputter deposition techniques is almost limitless. These methods of material synthesis do not suffer the limitations of bulk thermal dynamic equilibrium as conventional metallurgical methods. Earlier work with aluminum/aluminum oxide laminates[1] and tantalum/tantalum carbon laminates[2] produced by vapor deposition exhibited large and predictable strength increases by pulsing in oxygen and acetylene respectively. The yield strength followed a Hall-Petch dependence where the characteristic dimension was the spacing between pulses. Both earlier investigations utilized an electron beam gun source where the vapor is best characterized as a uniaxial flux source and condensed normal to the substrate. A subsequent study[3] of the effect of the pulsed gas process (PGP) on a rotating cylinder using the uniaxial flux source produced results indicating that grazing incidence flux causes self shadowing and a rough, voided, brittle coating to be produced. When the angle of incidence of vapor was reduced on the rotating cylinder, a set of conditions using the PGP could be found that produced a void free, [illegible], high strength coating. However, the conditions imposed by the masking on the angle of incidence limit the geometries that can be conveniently coated to obtain high quality coatings. Only two simple geometries, the cylinder and sphere, may be easily masked to produce the necessary conditions.

This limitation prompted the present investigation as it was thought that the use of an extended source would provide multiple angles of incidence present at the substrate *simultaneously*. Thus, instead of a time dependent angle of incident flux, as with the electron beam gun vapor source, the small fraction of grazing incident flux is always tempered with a majority of normal incident flux. In addition, it was of interest to know if another barrier material, such as AlN would provide the same properties as the oxide. The production of the nitride by sputtering[4,5] is very easily done. However, since the nitrogen does not chemisorb on aluminum at room temperature in the electron beam gun source, it is only conveniently made using the sputter technique. For conventional sputtering methods the mean free path of the sputtered atoms is ~ 1 cm or less, thereby, making the deposited atoms essentially thermalized. This makes the conditions of condensation similar to the uniaxial flux source with the variation that no element of substrate area ever "sees" a directional source.

Experimental

The sputter source used was a Plasmax triode gun that was subsequently magnetically enhanced to increase the deposition rates. The chamber pressure was maintained at ~ 0.8 Pa of argon during the runs using a Millitorr gauge and a pressure controller. A simple set of timers and counter were used to pulse in the nitrogen and to record the number pulses during a given run. The typical operating parameters were ∿ 100 V and 7-8 A used for the plasma current. The target was operated at ∿ 600 V with currents ∿ 1.3 A. The gun is shown schematically in Fig. 1. The condensation distribution of the source was measured at 10 cm from the front of the gun. The observed distribution is shown in Fig. 2. The uniformity of the deposit over this area shows the desired property of the extended source.

The freestanding films were deposited on glass slides ∿ 10 cm from the target. To obtain the foils, a thin layer of CsI was first evaporated on the glass, the run completed and the foils removed in water. The samples produced on the rotating cylinder were done in the geometry depicted in Fig. 1. The cylinder was first coated with CsI, followed by Al coating and subsequent removal in water. The nominal coating rate was ∿ 1.5 nm/sec for all the experiments. The nominal film thickness for both the flat plate and curved experiments was 5 μm.

Results and Discussion

An initial set of experiments was carried out to determine the effect of the nitrogen pulsing on the aluminum deposit. Figures 3a and 3b show the difference between a 2 μm deposit made at ∿ 5 cm from the target; 3a shows the SEM of an unpulsed coating and 3b shows a coating produced by pulsing every

~ 100 mm with nitrogen. The difference in surface roughness is dramatic. Figure 3c shows the growing surface of 30 μm thick pulsed film. Note that this growing surface is still smooth after eight hours of deposition! Figure 3d shows an SEM cross section of a fracture of the 30 μm specimen. The essential structure of this coating is lamellar rather than columnar. Auger Electron Spectroscopy and depth profiling are seen in Fig. 4. The periodicity of the nitride is well maintained and the ringed patterns reminiscent of the earlier work with the oxide.[1]

The mechanical properties of the foils are shown in Fig. 5. The yield strengths were measured on a special tensometer and the σ_{ys} taken at the 0.2% elongation value. The overall ductility of the samples was much lower than observed with the electron beam deposited samples. The total ductilities were ~ 1-2% at fracture. A log-log plot of the yield strength versus pulse spacing resulted in slope of -½. This gives the Hall-Petch equation for the yield strength shown in Fig. 5. Also plotted in Fig. 5 is the equation and curve for the vapor deposited Al/Al_2O_3 films for reference. It should be noted that the behavior of the two materials differ significantly in the flow stress, σ_o. It is suggested that the difference in flow stress is due to the possible grain refinement as a result of the multiple angles of incidence. The value of the constant K and the variation of strength with spacing remain essentially unchanged. The result for the pulsed cylinders are also plotted in Fig. 5. Note that these results indicate that there is no degradation in the mechanical properties as observed on curved surfaces in the uniaxial flux case.

An additional speculation about the high flow stress of the unpulsed material was that the target contained some unexpected impurity. A simple check was made by thermally evaporating a small piece of the target onto a glass substrate. Auger and Secondary Ion Mass Spectroscopy (SIMS) analysis showed no high level impurity in either the film or the remaining material. The evaporation was done to distill and concentrate higher and low vapor pressure materials for ease of identification. The films were also checked for residual argon entrapment by depth profiling with Xe. The argon content was found to be less than 0.2 at%. As a result, the high flow stress must be a result of the grain refinement and resulting structure of the film and not due to some alloying element.

Conclusions

High strength coatings of Al/Al+AlN have been produced using the PGP in a DC sputtering system. The yield strength follows a Hall-Petch relationship with a much higher flow stress and reduced ductility over films produced by uniaxial flux source. The curved surface experiment indicates that as long as a distributed source is used, masking is unnecessary for the angle of incidence deposits. The addition of the pulsing to the curved cylinder deposits increases the strength without any degradation.

The significance of this work is that high quality coatings may be made on arbitrary geometries without the use of masking. A possible strong candidate of an ideal source is the inverted Thornton[6] magnetron. The conditions of an extended source would be easily fulfilled. In addition, the use of an impurity gas may not be required to provide a perturbing layer with this magnetron. A change in sputtering pressure, as reported by Thornton[7] alters the coating properties such as the sign of the film stress and the optical reflectance. It may be possible to obtain the same effects as the PCP by simply toggling the pressure to move from Thornton's zone T to the more classical zone observed in conventional sputtering pressure.

In conclusion, the extended source used in sputtering has been found to produce excellent material on flat as well as curved substrates. The yield strengths are governed by the spacing of an impurity incorporated during film growth.

Figure Captions

Figure 1 The triode sputter gun and rotating cylinder are shown schematically. The stray flux shields ensure that any grazing incidence flux is tempered with a component of normal incidence flux. The aperture spacing is about 10% wider than the cylinder diameter.

Figure 2 The flux distribution over the front of the target is plotted. The smooth variation and uniformity provide a good extended source characteristic. The data was obtained ~ 10 cm from the target.

Figure 3 Scanning Electron Micrographs of various surfaces are shown. All micrographs were taken at the same magnification. a) The surface two micron pure aluminum deposit is shown in contrast to a pulsed aluminum coating in b. c) The surface of a ~ 30 micron pulsed foil is shown. Only faint morphology can be seen in the SEM, not visible to the unaided eye. d) A fracture surface of the 30 micron foil is shown to illustrate the lamellar rather than columnar structure.

Figure 4 An Auger Electron Spectroscopy depth profile detailing the nitrogen and oxygen concentrations is shown.

Included for reference is an SEM image of the sputter crater and a Scanning Auger Micrograph of Nitrogen of the inset. Note that the oxygen profile zeros very rapidly and that the nitrogen is uniformly repetative with essentially zero nitride between pulses.

Figure 5 The yield stress as a function of layer spacing is plotted. The yield strength found for the Al/Al_xO_y is plotted for a reference. The essential difference in the curves is the value of the drag stress, σ_o. The open circles are the values of yield stress obtained from the rotating cylinder. The yield strengths are not degraded as with the oxide coatings.

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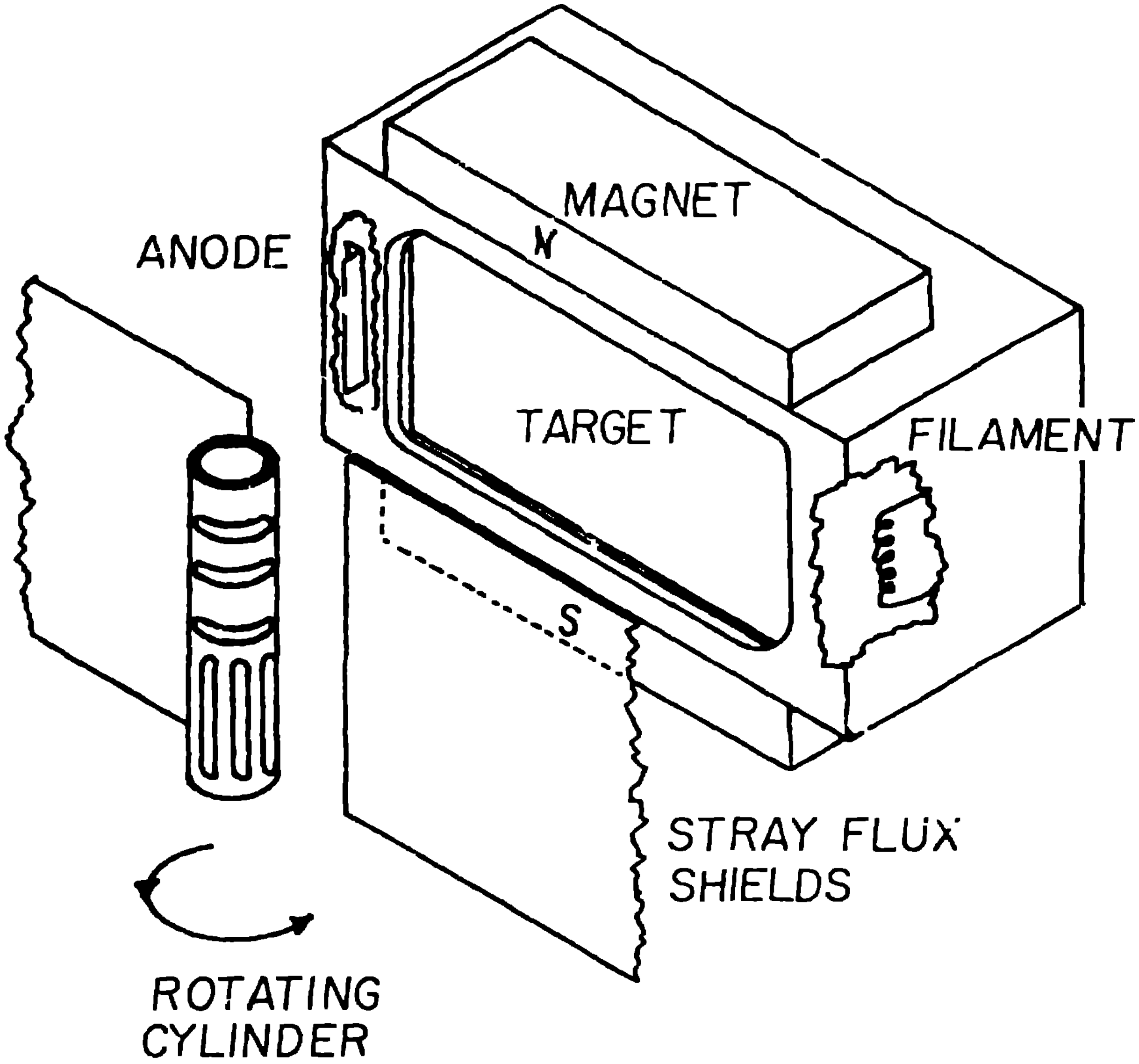
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N
ANODE
TARGET
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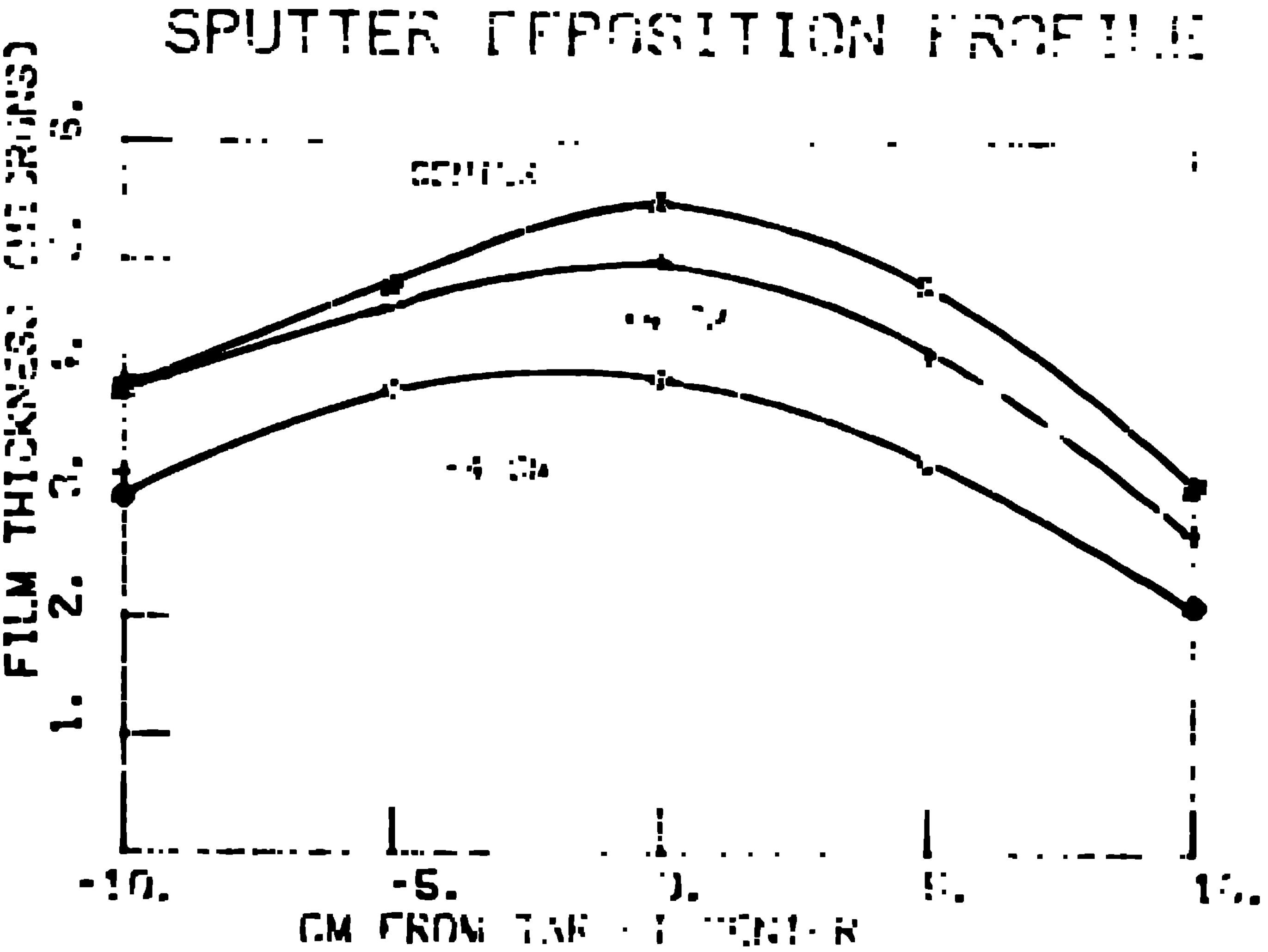
ROTATING
CYLINDER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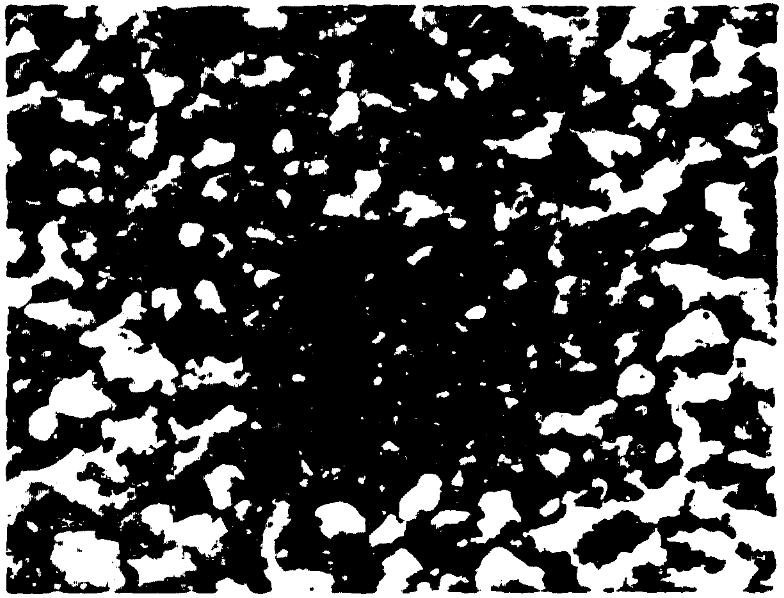
1.
2.
3.
4.
5.
CENTER
+4 CM
-4 CM
-10.
-5.
0.
5.
10.
CM FROM TARGET CENTER



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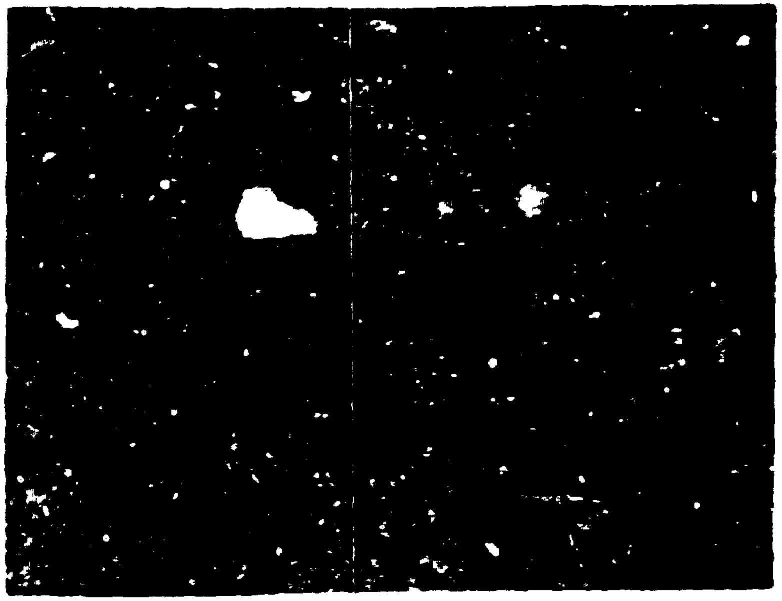

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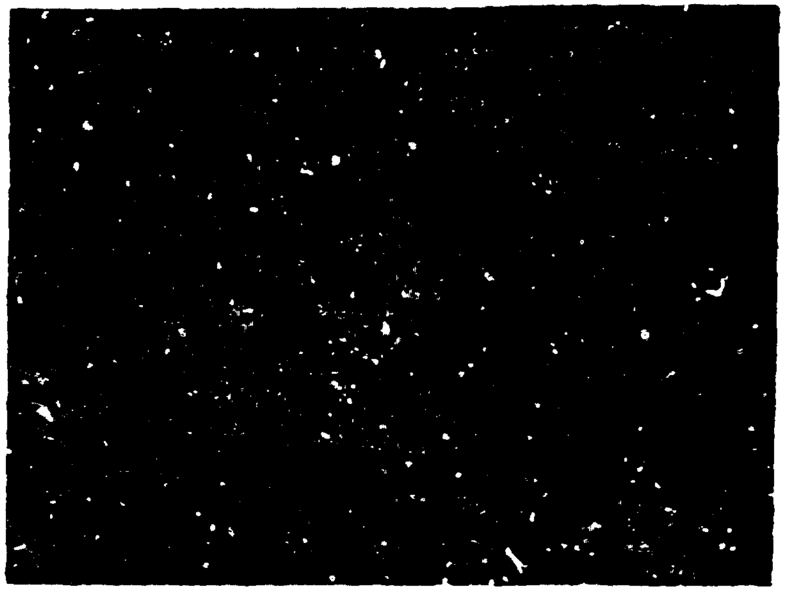

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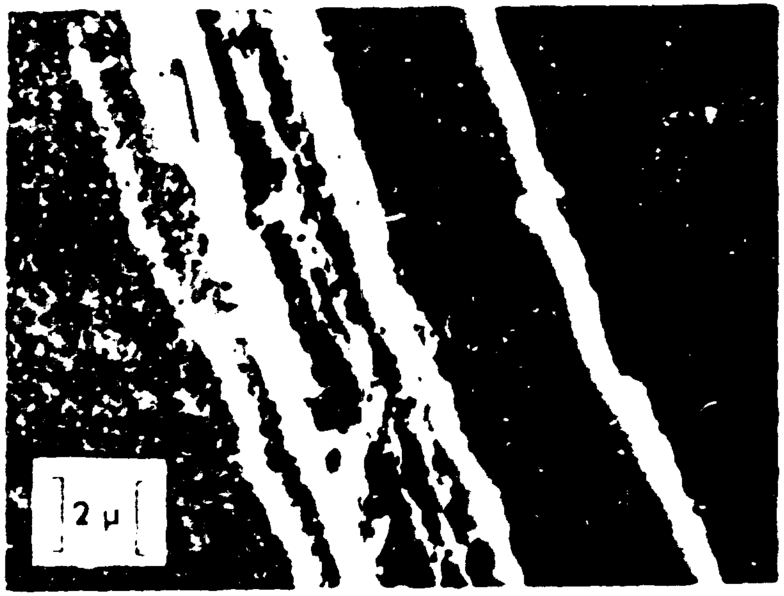

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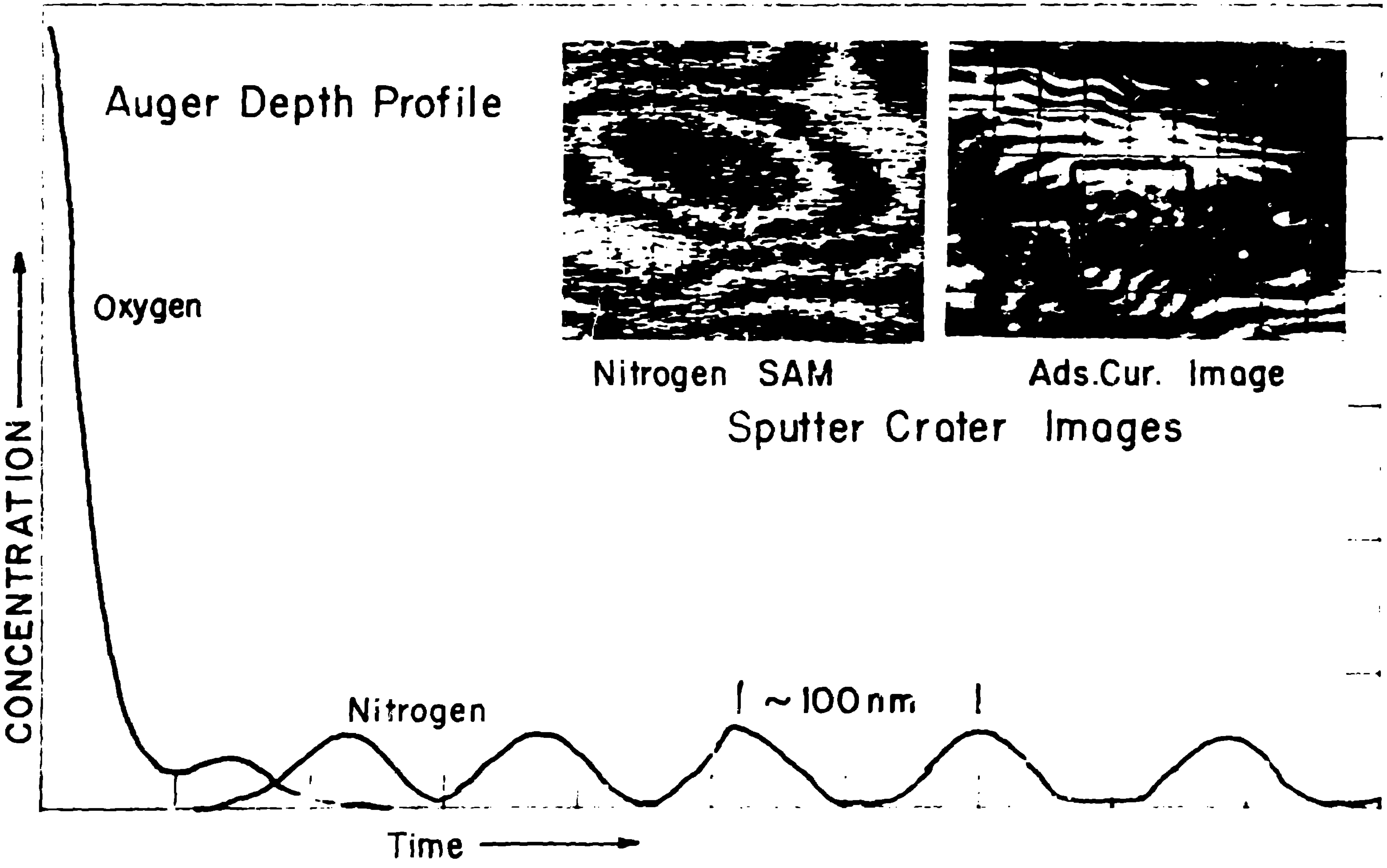
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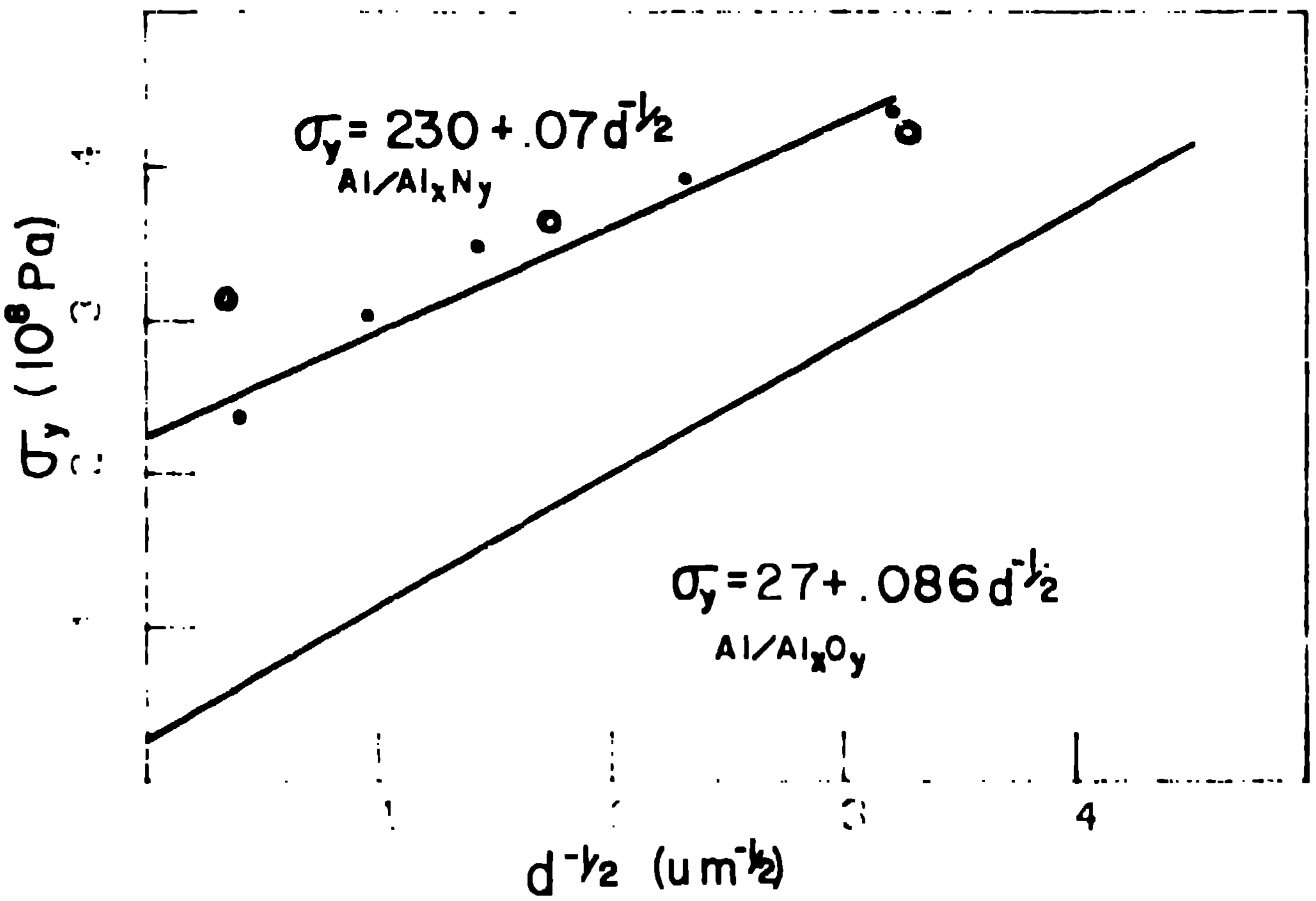
Nitrogen
~100nm
CONCENTRATION
Time


$\sigma_y = 230 + .07d^{-1/2}$
Al/Al$_x$N$_y$
$\sigma_y = 27 + .086d^{-1/2}$
Al/Al$_x$O$_y$
σ_y (10^8 Pa)
4
3
2
1
2
3
4
$d^{-1/2}$ (um$^{-1/2}$)