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Cathodes for HeNe Lasers

Vapor deposited aluminum cathodes for parallel plate HeNe lasers have been used with considerable success. It is shown that the aluminum cold cathode is improved by the addition of copper and that other alloying elements of bulk Al 2024 do not contribute to cathode performance. The plasma oxidation process of Hochuli improves cathode performance by cleaning the surface and optimizing the oxide film for maximum efficiency. There appears to be a trade-off between life and electron tunneling efficiency for optimum oxide thickness. Auger electron spectroscopy, ellipsometry, and scanning electron microscopy are the techniques used for surface characterization.

Introduction

An electron-emitting surface or cathode, required for a dc glow discharge, provides a continuous source of new electrons replacing those lost by the plasma. Several techniques used for energizing the cathode are described in the extensive literature on cathodes for electron devices [1-3]

In the thermal electron emitter, the cathode is heated so that sufficient energy is imparted to a certain proportion of electrons, which are then able to overcome the work function of the material. An electric field is used to accelerate the electrons away from the heated surface. Tungsten, tantalum, and metal oxides are commercially significant for use as cathodes in electron tubes. Cold cathodes are made from metals such as Al, Be, and Ta [4-6], which form thin adherent oxides. They emit mostly secondary electrons produced by ion bombardment of the oxide surface. Porous oxide is also used, but it depends on the Malter effect [7-9] for operation. A high electric field is applied across the thin porous oxide, and electrons are accelerated across the film and emitted.

The geometrical configuration of cathodes is known to have considerable effect on life and other operating characteristics. A configuration such as the hollow cathode ensures the return of particles in the plasma to the cathode. Although there may be a high sputtering rate, little is lost from the cavity. The burying of gas molecules in sputtered material has been shown to be self-limiting, and very high current density has been obtained for almost spherical hollow cathodes [10]. A study of the cylindrical hollow cathode for the HeNe laser, with the objective of optimizing geometry, was made by Martynov et al. [11].

HeNe lasers operate at relatively modest current densities, less than 500 mA/cm^2, in a bore less than 2 mm in diameter. A total current of less than 10 mA is necessary for lasers providing up to 25 mW of output power. When the cathodes are operated at these current levels in HeNe gas at 2 to 4 mm Hg, Hochuli et al. [4, 5] have shown that aluminum cold cathodes have longer life than other cold cathode materials and all hot cathodes tested. Since their papers were published, the aluminum cold cathode has become standard in the HeNe laser industry. According to the method of Hochuli et al., Al 2024 T351 is machined using distilled water as a coolant and then cathodically treated in a plasma of 2.7 $\times$ 10^2 Pa of oxygen at 5 to 10 mA/cm^2 of active surface. Other Al alloys and dif-

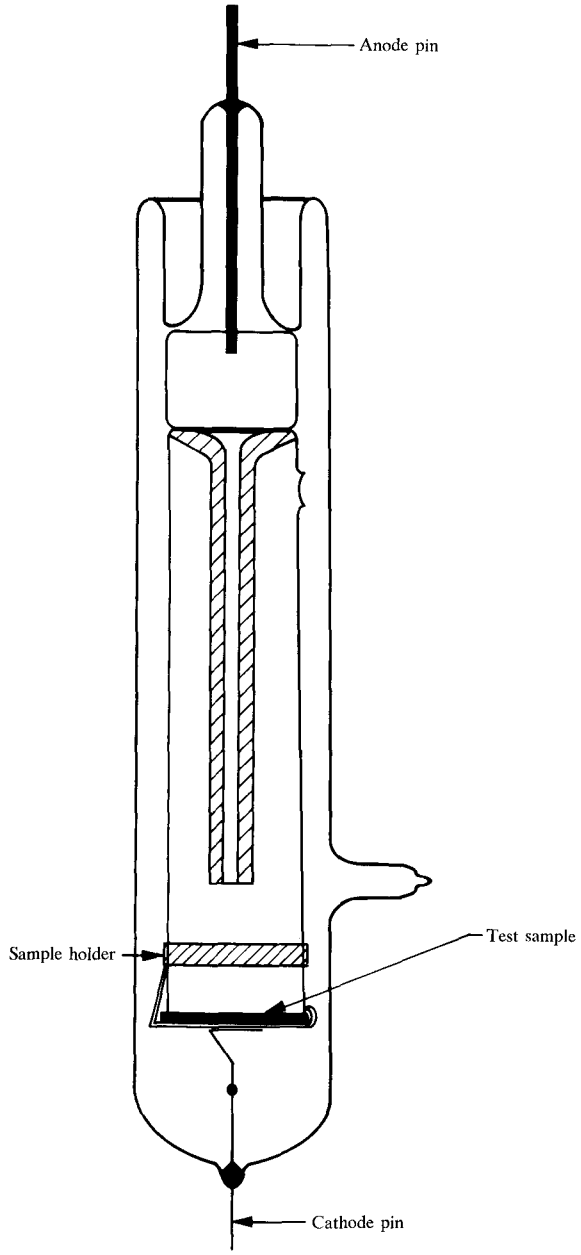

Figure 1 The tube life test cell.

ferent processing conditions are being used successfully, as close inspection of commercially available lasers shows.

Deposited film cathodes have many advantages in the fabrication of the parallel plate HeNe laser [12, 13]. Electrical feed-throughs may be fabricated as extensions of the deposited cathode and subsequently isolated from the cathode chamber by seal glass. The material deposited and the deposition process can be effectively controlled. Gas evolution from the film material is negligible, and the smooth surface of deposited cathodes can be analyzed more easily than the rough surface of machined or etched cathodes.

Experimental work

The purpose of the experimental work presented in this paper was to obtain an understanding of the effect of processing parameters on the aluminum cathode surface and to develop a practical thin film aluminum cold cathode which would operate reliably for several thousand hours. We also wanted to correlate materials and processes which result in good cathodes with the surface characteristics of such cathodes. Emphasis was placed on identifying the essential alloying elements of Al 2024 (4.4% Cu, 1.5% Mg, 0.6% Mn), if any, and on the use of a smooth surface.

Thermal and electrochemical oxidation of Al has been studied extensively [14–16]. Dc plasma oxidation of thin bulk Al by electron transmission metallography was reported by Ignatov [17]. More recently, rf oxidation at the cathodes made of other metals was reported [18], and new techniques were developed for the analysis of thin films. Thermal and dc plasma oxidation of the cathode occurred in the fabrication of a parallel plate laser, and we wanted to analyze the effect of these processes on Al. Ellipsometry, Auger electron spectroscopy (AES), and scanning electron microscopy (SEM) were the methods used to determine oxide thicknesses, compositions, and morphology.

Sample preparation

Cathodes for oxide and life studies were prepared with and without the alloying elements of Al 2024. The films were pure aluminum or aluminum alloys deposited by successive e-beam evaporation of Al/alloying constituent/Al. They were 1 to 3 μm thick and were deposited on glass substrates preheated to 140 or 200°C. The samples were then annealed at 500°C for one hour in He. Because of the rapid diffusion of the alloying elements in Al, the samples were homogeneous after annealing. The latter fact was verified for Cu by comparing layered samples of Al/Cu/Al with similar compositions obtained by dual e-beam evaporation.

Bulk materials were cut from bar stock to the shape of disks. They were then ground and polished with 0.3-μm Al_2O_3 particles.

Life tests

The cathode test cells shown in Figs. 1 and 2 were used in the determination of cathode life. The tube cell shown in Fig. 1 was fabricated from Pyrex glass (C7740). The cath-

ode of the cell, either bulk or thin film material, was mounted perpendicular to the current flow, and the plasma was constrained within an area of 4 cm^2. The bore through which the current flowed was one mm in diameter, its length was 90 mm, and its distance from the cathode was 25 mm. The anode was a tungsten wire sealed through the Pyrex tube.

In the parallel plate cathode cell shown in Fig. 2, both the anode and cathode were evaporated onto the lower glass plate. The middle section had one-inch-diameter holes which served as the cathode and anode chambers. The connecting bore between the two chambers was a one-mm square channel cut into the top side of the middle plate. A hole was drilled in the top plate above which was attached the tip-off tube. The dc current for plasma oxidation and gas filling were carried out through this tip-off tube. When all three plates and the tip-off tube were sealed together by means of the seal glass [19], the test cell was completed except for tip-off.

In the typical preparation for life testing, the cells were evacuated and then baked overnight at 200°C under a vacuum of 10^{-5} Pa. Each cell was subjected to plasma treatment in an oxygen atmosphere at a pressure of 2.7×10^2 Pa. The oxidation was carried out at a current density of 5 mA/cm^2 for various periods and was conducted in 5-minute cycles. After each cycle, the cell was evacuated and refilled with oxygen. The total oxidation times are shown in Table 1. After the oxygen treatment, the cells were evacuated and then filled to the desired pressure with a mixture of seven parts He^4 to one part Ne^{20}. They were then operated with the HeNe plasma, evacuated, refilled with HeNe, and tipped off. Life tests were carried out at a current of 2 mA, which gave an average current density over the cathode surface of 0.5 mA/cm^2. The maximum current density of 0.52 mA/cm^2 for the parallel plate cell was estimated by assuming a linear current distribution as a function of radius from the bore. The method of calculation is illustrated in Fig. 3.

Surface analysis

Changes in the surface of Al thin films and bulk Al samples after deposition or preparation and after various process treatments were observed and evaluated. Examination by scanning electron microscope showed gross changes such as those affecting surface topography and grain size. Oxide thickness changes were measured by means of ellipsometry. Finally, Auger electron spectroscopy with sputtering capability was used to obtain the relative oxide thicknesses and composition of the oxide films. The samples tested are listed in Table 2. The samples, whether thermally oxidized or not, were mounted in the AES system and rotated opposite to the port for plasma treatment. After treatment, the samples were again rotated in position for Auger analysis and profiling. The plasma treatment arrangement is schematically shown in Fig. 4.

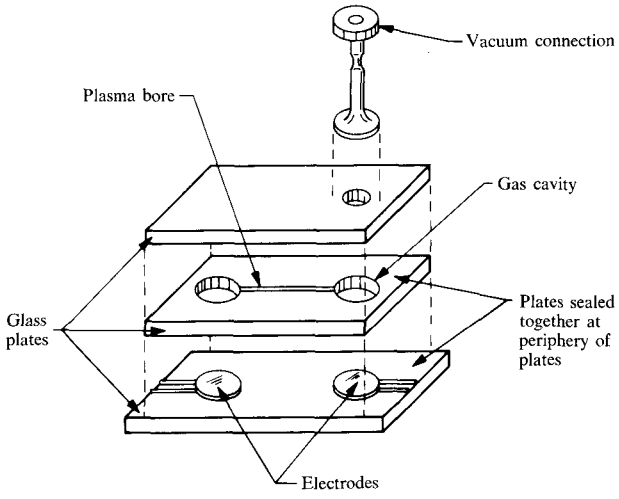

Figure 2 The parallel plate cathode cell.

Table 1 Cathode life test results.

Cell type	*Material*	*Cathode oxidation time* (min)	*Time to failure* (h)	*Other*
Parallel plate[a]	Al	0	82	film sputtered
	Al	30	408	film sputtered
	Al-1.5% Mg	0	130	film sputtered
	Al-1.5% Mg	30	768	film sputtered
	Al-4.5% Cu	0	221	film sputtered
	Al-4.5% Cu	30	2424	film sputtered
	Al-33% Cu	0	1776	film sputtered
	Al-33% Cu	30	1586	film sputtered
	Al-54% Cu	0	116	film sputtered
	Al-54% Cu	30	116	film sputtered
	Al 2024[c]	10	60	sputtering detectable
Tube[b]	Al-4.5% Cu	10	<200[d]	film sputtered
	Al-4.5% Cu	15	8800	film sputtered
	Al-4.5% Cu	20	2068	film sputtered
	Al-4.5% Cu	30	287[d]	film sputtered
	Al 2024	10	2000	sputtering detectable
	Al 2024	20	4500	sputtering detectable
	Al 2024	30	3800	sputtering detectable

[a]Maximum current density during life test = 0.52 mA/cm^2.
[b]Average current density during life test = 0.5 mA/cm^2.
[c]Bulk material. Maximum current density higher owing to bulk thickness.
[d]Tubes developed leaks.

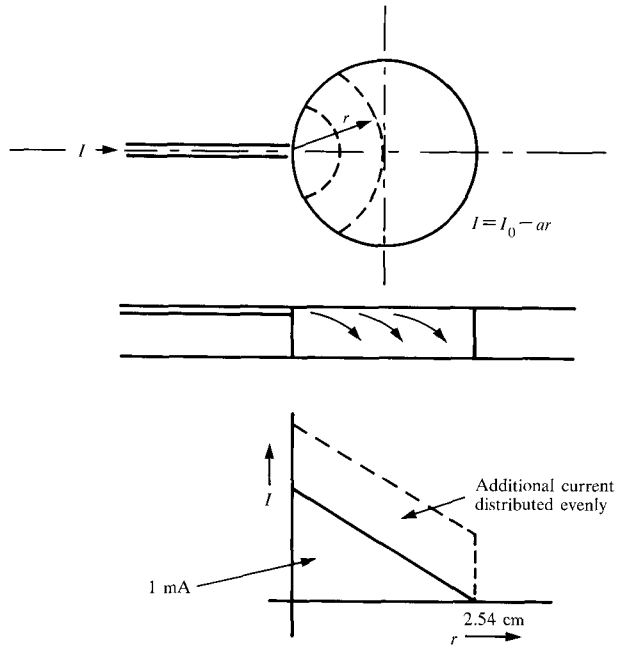

Figure 3 Schematic representation of the bore entry, cathode cell, and current distribution (assumed to be linear as a function of radial distance from the bore).

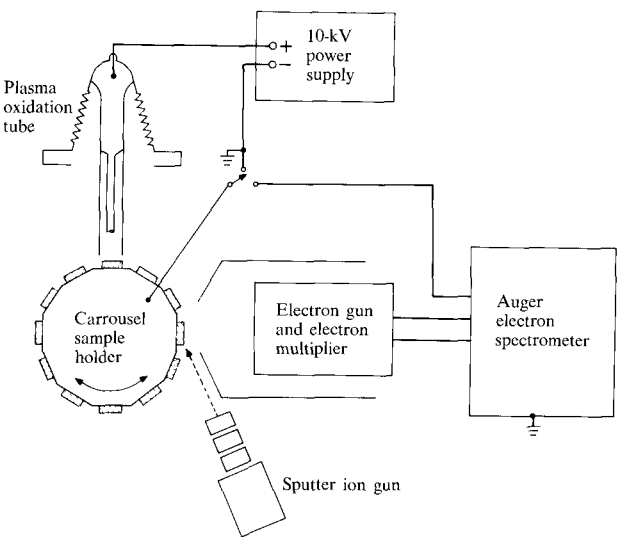

Figure 4 Schematic representation of the plasma treatment arrangement attached to the Auger system.

Results and discussion

An initial experimental matrix determined which alloying constituents of Al 2024 were present in the oxide after thermal and cathodic dc plasma oxidation. Al, Al-Cu, Al-Mg, Al-Cu-Mg and Al-Cu-Mg-Mn (Al 2024) samples were analyzed. Auger analyses showed Cu as the only detectable (<0.1%) alloying constituent in the oxide. We then proceeded to optimize the Cu content and processing conditions for best life.

Optimum composition and plasma treatment

The results of pertinent life tests as functions of material compositions and processing conditions are summarized in Table 1. Al-4.5% Cu was determined to be a cathode which was close to optimum. A synergistic effect by the elements in Al 2024 was not found. Al-1.5% Mg showed marginal improvement over a pure aluminum cathode.

The experiments in the tube cell served to optimize the plasma treatment time for both thin film Al-4.5% Cu and bulk Al 2024 cathodes. The results indicate that approximately 15 minutes of plasma treatment at 5 mA/cm^2 is optimum. The tests also showed that the thin film, smooth surface cathode is as good and perhaps better than the bulk aluminum (Table 1).

Oxide thickness

Oxide thicknesses on Al and Al-Cu samples were determined by ellipsometry after thermal oxidation and cathodic plasma treatments. To obtain the data shown in Table 2, samples were processed in an inert atmosphere or in oxygen for 60 minutes at 500°C and by a cathodic dc plasma treatment as indicated. The cathodic treatment selected for these measurements was 15 minutes at 5 mA/cm^2. With an initial native oxide thickness of 2 to 2.5 nm, oxide thicknesses on pure Al grew to over 10 nm after thermal treatment in oxygen and to approximately 5 nm in the inert atmosphere. The change in oxide thickness was also observed to be a function of Al composition and method of deposition.

The effect of cathodic dc plasma oxidation was small, and measured changes were of the order of 0.5 nm. The change in oxide thickness was observed to be dependent upon the oxide thickness prior to the treatment. Thick oxides (greater than 10 nm) were reduced in thickness, whereas thinner oxides (<5 nm) grew. These results for Al were similar to steady state oxide thicknesses observed by Greiner [18] for rf oxidation of Pb. It appears that cathodic dc plasma treatment produces oxide thicknesses between 5 and 8 nm, which result in the maximum cathode life.

Surface morphology

SEM photographs were useful in identifying phase formations and grain boundary changes owing to thermal and cathodic oxidation treatments. For the Al thin film surface as deposited at 140°C, plasma treatment did not result in any apparent change. Figure 5 shows the Al surface after treatment in O_2 at 500°C. A similar surface was

Table 2 Matrix of test samples.

Material	*Sample number*	*Thermal treatment 500°C in*		*Plasma oxid. 270 Pa*	*Ellipsom. oxide thickness change* (nm)	*SEM*	*Auger*
		Inert	O_2				
Al[a]	1					x	x
deposited	2			x	1.35		
at 140°C	3	x			2.59		
	4	x		x	3.14		
	5		x		8.41		
	6		x	x	8.01		
Al-4.5% Cu[a]	7			x	1.20		
deposited at	8	x			7.53		
140°C	9	x		x	7.37		
	10		x		7.81		
	11		x	x	7.59		
Al-4.5% Cu	12			x	1.62		
dual hearth deposited	13	x			1.09		
at 140°C	14	x		x	2.08		
	15		x		1.63		
	16		x	x	2.03		
Al 2024	17			[b]	[c]		
	18						
	19	x					
Al 6061	20			[b]			
	21	x					

[a]Sample set duplicated at 200°C deposition.
[b]Three plasma oxidation conditions.
[c]Not measured.

observed after treatment in N_2. These thermal treatments in both atmospheres resulted in grain delineations, and further oxygen plasma treatments resulted in no apparent change.

The result for Al-4.5% Cu layered film is shown in Fig. 6. A similar surface was observed for Al and Cu evaporated simultaneously from separate hearths. Grain delineations and depressions observed for pure Al were less widespread than for Al-Cu, indicating less restructuring in the Al film. The bright spots are the result of θ-phase formation in the Al-Cu matrix and can be attributed tc higher secondary-electron emissions from these areas.

Surface composition

Auger profile analyses are shown in Fig. 7 for the layered film of Al-4.5% Cu. The profiles shown are for Al and Cu after thermal treatment in oxygen at 500°C and after cathodic plasma treatment. The following observations were made:

1. Cathode plasma treatment reduced the thickness of the oxide grown by thermal oxidation.
2. Copper was detected throughout the oxide film.

The first observation confirmed the thickness change already shown by ellipsometric measurements. In the second, it is not clear whether copper is located only in oxides over the θ-phase of Al-Cu or whether the copper is distributed throughout the oxide.

The relative oxide thickness was determined from the length of time required to sputter through the oxide. It was evident in these experiments that there were differences in the oxide thickness or resistance to sputtering. In bulk Al 6061 (0.6% Si, 0.27% Cu, 1% Mg, 0.2% Cr), Al 2024, and some evaporated films, the oxide/Al interfaces were sharply defined. This was in contrast to the interfaces of other evaporated films which were thermally oxidized in O_2 at 500°C. In the latter cases, the oxides were porous or were difficult to etch. Table 3 shows the observed relative oxide thicknesses for bulk and evaporated films.

In the case of bulk Al 6061, a minimum plasma conditioning time between 10 and 20 minutes was necessary for the oxide to grow to a thickness which did not change significantly with further treatment. For the Al 2024, 5 minutes of plasma treatment was sufficient time to

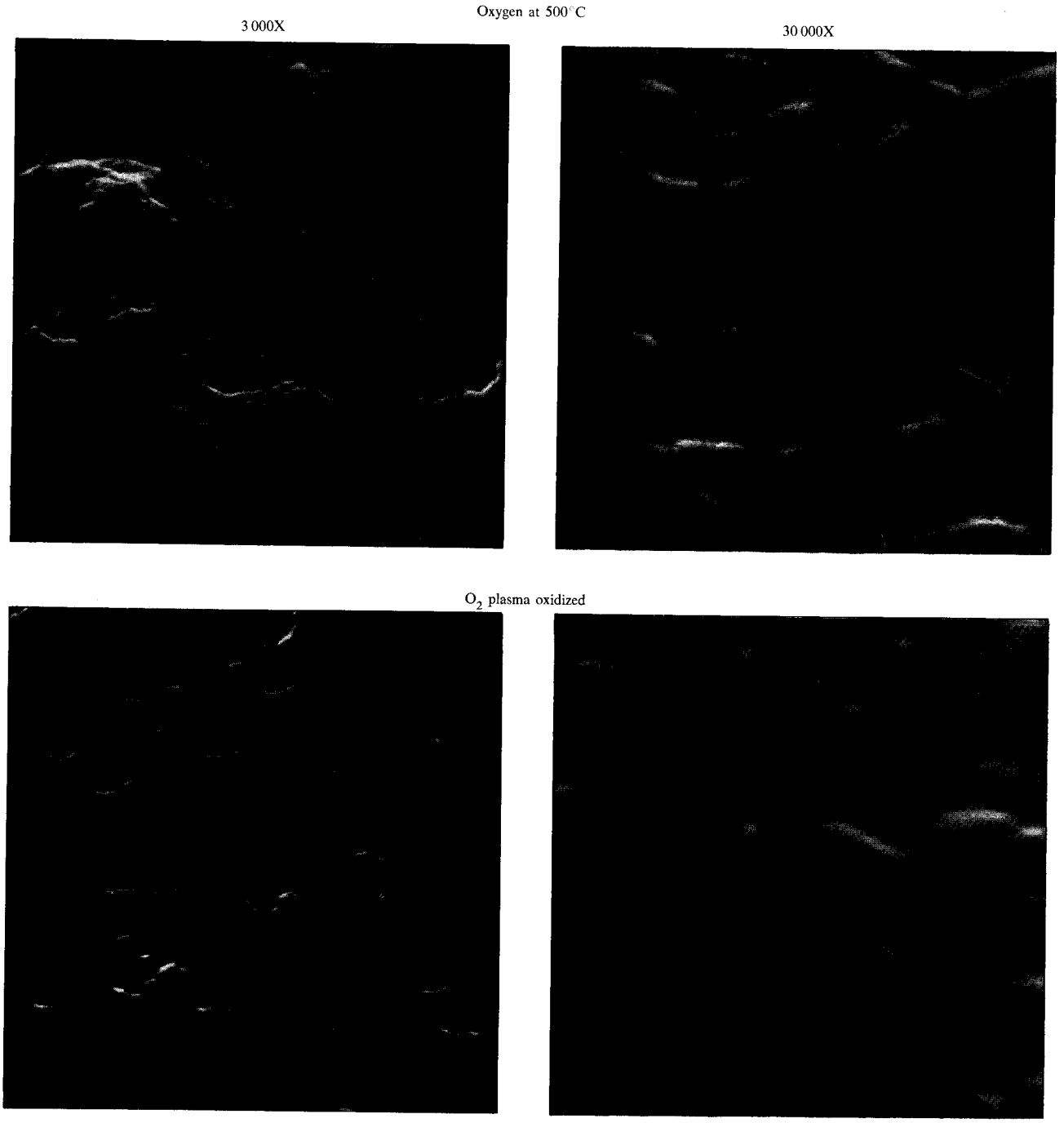

Figure 5 SEM photograph of Al thin film after oxidation in oxygen at 500°C and subsequent plasma treatment.

achieve this level of thickness. This result may be evidence that Al 2024 is a more "forgiving" material in achieving a stable condition and better reproducibility in the life studies.

Conclusions

Al cold cathodes used in HeNe glow discharge show life of thousands of hours even with smooth surfaces at relatively high current densities (~0.5 mA/cm^2).

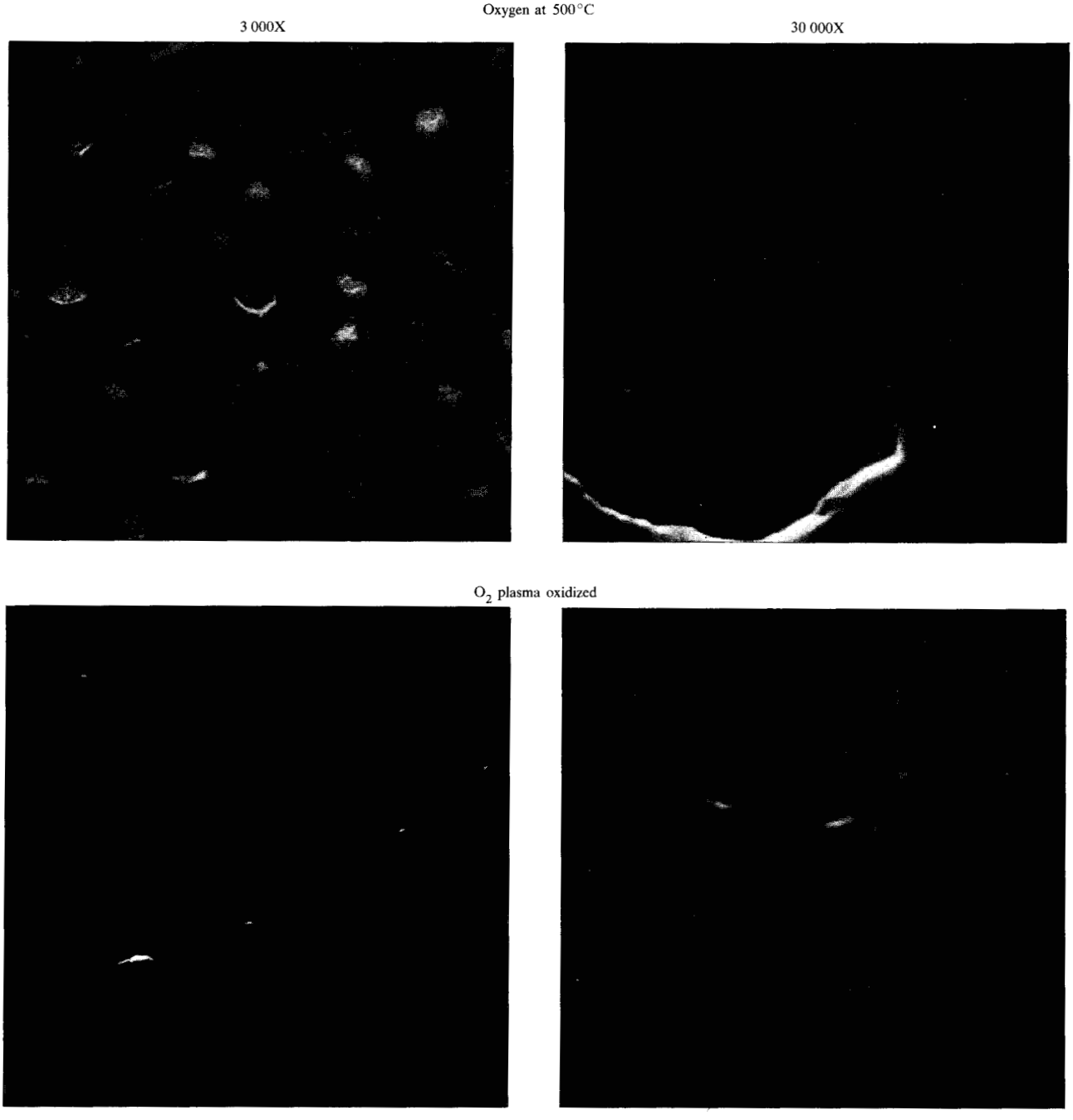

Figure 6 SEM photograph of aluminum/copper/aluminum deposited at 140°C, heated in oxygen at 500°C, and then plasma oxidized.

Cathodes fabricated with 1-3-μm evaporated films are as good and may even be better than bulk Al cathodes. With optimum material and cathodic oxygen treatment, the indications are that thin film cathodes are superior.

Cathodic dc plasma treatment in oxygen cleans the surface of the cathode and tends to optimize the oxide thickness for cathode operation in a HeNe plasma. The optimum oxide thickness for good life is between 5 and 8 nm.

Table 3 Relative oxide thickness (as indicated by sputter time in minutes).

Sample	*As deposited or polished*	*After 1 h 500°C N_2*	*After 1 h 500°C O_2*	*After in-situ plasma oxidation in oxygen at 270 Pa*				
				5 min 5 mA/cm²	*10 min 5 mA/cm²*	*15 min 5 mA/cm²*	*20 min 5 mA/cm²*	*5 min 15 mA/cm²*
Al 2024	4			19.5	17.8		25.2	
Al 6061	6.5			6.5	6.8		25.2	6.5
Al film (140°C)	21.5	28	35			46[a]		
						60[b]		
Al/Cu/Al (140°C)	18.5		>60			53[b]		
(200°C)	20.2							
Al-4.5% Cu dual hearth deposited at 140°C	24.2		43.2			35		
						45.4[b]		

[a] Plasma oxidation after 1 h at 500°C in N_2.
[b] Plasma oxidation after 1 h at 500°C in O_2.

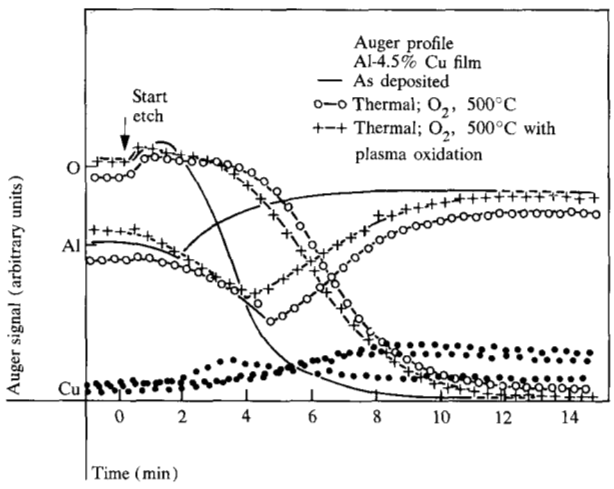

Figure 7 Auger profile analyses for Al-4.5% Cu layered film.

The alloying constituent Cu is desirable in the fabrication of Al cathodes for better reproducibility, sputter resistance, and life. Al alloyed with 4.5% Cu achieves a stable oxide thickness and optimum oxide conditions more readily than pure Al or Al with other alloying elements. For these reasons Al 2024 is preferred to Al 6061.

The experimental results show longer sputter times for the removal of oxides from evaporated films than from bulk materials. This is an indication of thicker oxides or better resistance to sputtering. The results are also additional evidence to support superior life obtained on evaporated films.

Oxide layers thicker than 5 to 8 nm, as may be obtained by thermal treatment, are detrimental if poor conductivity prevents electron emission. The data indicate that some thermal oxidation followed by plasma treatment, both in oxygen, should result in the best life for the evaporated film cathode.

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