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SAND95-2179C

Healing Defects in Anodic Aluminum Oxide Coatings Using Sol-Gel Materials - A Screening Study Using the Product of Capacitance and Breakdown Voltage as a Figure Of Merit

(SEMATECH ESC S-59G PROJECT - AUG. 31, 1995)

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ABSTRACT.

Thick, hard or clear anodic aluminum oxide films are often used as dielectric coatings on commercial electrostatic chucks. These devices are produced with low yield, and their performance is erratic in practice; for this reason, cost effective methods of improving the electrical properties and homogeneity of the thick, porous anodic films are being sought. We have studied sol-gel coatings on anodic films, and have shown that some sol-gel coatings improve the electrical properties of anodic films while others degrade them. High density silica applied to anodic films by dip-coating using a sol bath gave composite films with the best quality, homogeneity and process reproducibility. Anodic films coated with alumina-silica deposited by double dip-coating or with silica electrophoretically deposited from a low water content sol also had improved properties.

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ACKNOWLEDGMENT

This work was performed at Sandia National Laboratories, supported by the U. S. Department of Energy under contract number DE-AC04-94AL85000.

1. EXECUTIVE SUMMARY.

Some sol-gel coatings improve the electrical properties of anodic films while others degrade them. High density silica applied to anodic films by dip-coating in a sol bath gave composite films with the best quality, homogeneity and process reproducibility. Anodic films coated with alumina-silica deposited by double dip-coating or with silica electrophoretically deposited from a low water content sol also had improved properties.

2. INTRODUCTION.

Anodic aluminum oxide coatings are used in the microelectronics industry in two important ways:

1. As electrostatic chuck dielectric coatings and
2. As corrosion resistant dielectric coatings in plasma-assisted etch and chemical vapor deposition tools.

Cracks, pores and flaws in these coatings degrade their performance.

Sol-gel coating can apparently heal anodic film porosity, cracks and flaws, leading to more homogeneous films. In this study some anodized aluminum samples were coated by dipping them into sol dispersions, then drying and heat treating the deposited material. Other anodized samples were coated using an electrophoretic technique, in which sol particles were driven to the sample surfaces using an applied electric field. Sol-gel coatings can improve or degrade dielectric properties of samples, the effect depending on the anodic coating microstructure and the sol-gel material and coating procedure. Dip-coating high density silica sols led to high quality, homogeneous composite coatings; results weren't sensitive to processing conditions. Another process using two dip-cure cycles with an alumina-silica sol also gave promising results. Finally, electrophoretically depositing a relatively high density silica sol-gel on anodic coatings gave good results.

3.0 EXPERIMENTAL.

3.1. Anodic Coatings.

Anodic coatings approximately 38 micron thick were formed on 51 mm diameter, 1 mm thick discs of 6061-T6 aluminum alloy. These discs, stamped from a single mill run of rolled sheet stock, were prepared for anodization using a sodium hydroxide preliminary etch and a nitric acid desmutting final etch. A number of substrates were anodized in 14 wt% sulfuric acid at each of three processing temperatures to produce coatings with a range of porosities:

1. 17 to 20°C - nominally "20°C" - most porous,

2. 9 to 11°C - nominally "10°C" - intermediate porosity, or

3. 0 to 6°C - nominally "0°C" - least porous.

Two samples anodized at each of three temperatures were set aside with no further treatments as experimental controls. In addition, two samples anodized at each of three temperatures were sealed in boiling deionized water for thirty minutes and then set aside.

3.2. Sol-Gel Processing.

3.2.1. Sol-Gel Technology Introduction.

Sol-gel processing can be used to produce and give form to glass and ceramic materials at temperature far lower than those required for conventional processing of oxide powders. This technique can often be used to prepare bulk materials, fibers, and thin films when fused or sintered materials cannot meet process or product requirements. Successful commercial applications including sol-gel optical coatings for automobile mirrors (1950's) and architectural coatings (1960's) show that this is a robust manufacturing technology. More recent areas of application include energy and space systems, electronics, sensors and membranes.

Sol-gel chemists generally uses reactive monomeric compounds like metal alkoxides ($M(OR)_x$, where M is a metal and R is a low molecular weight alkyl group) as sol precursors. Monomers in an alcohol/water solution will undergo hydrolysis and condensation reactions to yield a network of inorganic polymer linkages (M-O-M). Control of these reactions in solution, i.e., by manipulation of pH, solvent composition and concentration, water to alkoxide ratio, modifying ligands, aging conditions, etc., dictates the type and extent of particle or polymer growth and influences the resultant microstructure. For example, weakly branched species are fairly compliant and form denser oxides; highly cross-linked polymers, in contrast, resist the compressive forces of surface tension during drying, leading to larger pores that can only be removed by high temperature sintering. The physics and chemistry of sol-gel processing have been extensively reviewed by Brinker and Scherer[1].

If the polymerization reactions are quenched before completion, the resulting "sol" can be used to deposit glassy coatings onto glass, ceramics, metals or plastics using a variety of coating methods such as dip-, spin-, roll-, and spray-coating and electrophoresis. The coating method chosen depends on factors like substrate geometry, substrate size, and sol properties (vapor pressure and surface tension of solvent, sol rheology, polymer structure, etc.). Dip-coating is an economical and simple method to deposit films onto symmetrical substrates (plates, tubes, disks). At Sandia, dip-coating has been used to deposit thin, uniform coatings on substrates ranging in dimensions from microelectronic devices (a few mm^2) and sensor probes (thin wire), to solar tubes (inside and outside of 3" diameter, 10 ft. long tube) and metal mirrors (2 ft. x 2 ft.). Spin coating is often used to deposit coatings onto one side of a flat, symmetrical substrate less than ~8" in its greatest dimension (e.g., a silicon wafer). Spray coating may be used to coat large or geometrically complex substrates for applications where precise coating thickness is not required (e.g., protective coatings on metals). Metered coating methods, where a controlled volume of solution is delivered to the substrate and precisely distributed over the surface, may be desirable for applications requiring continuous coating of a roll of material or minimal sol loss. An alternative to the above passive deposition methods is electrophoresis, in which sol particles or polymers are actively drawn to the substrate surface. Drying conditions, firing temperature and ramp rate, and firing atmosphere can also influence film shrinkage and cracking regardless of deposition method.

3.2.2. Processing steps used to deposit sol-gel coatings onto anodized aluminum.

Selected unsealed anodized substrates were coated with different sols. We focused our efforts on anodic films with substantial porosity (anodized in sulfuric acid at 10°C or 20°C). Table 1 shows the characteristics of samples prepared and characterized in this study. About half of each sample was immersed in the sol dispersion. The other half was left uncoated. Properties of films on sol-gel treated areas and the untreated areas were analyzed and compared; in this way we could determine which anodic film property changes resulted from sol-gel coating materials and which were the result of thermal treatments alone.

3.2.2.1 Cleaning.

Anodized samples were cleaned before coating in the following way:

(1) degreased in trichlorethylene vapor at 80°C,
(2) washed in a detergent-alcohol solution (6 l isopropanol, 1.5 l deionized water, 1.5 ml Triton-X100, 3.75 ml Span-80) for 15 minutes,
(3) rinsed in flowing deionized water,
(4) rinsed in hot deionized water (75°C, 2 min.),
(5) blown dry with nitrogen gas.

3.2.2.2 Pre-Heating.

Some samples were heated in air at a rate of 10°C/min. to 450°C for 15 minutes before depositing sol-gel coatings. This was done to rupture weak areas of the anodic films, opening paths into the film along which sols could penetrate. Heat treatment darkened the anodic coatings; microscopy showed the surfaces to be "mud-cracked".

3.2.2.3 Solution Preparation.

Details of sol preparations are given below; detailed information can be found in the references. Unless noted, all sols are indefinitely stable when stored at -20°C.

A2 is an acid-catalyzed SiO_2 sol prepared using the two-step hydrolysis/condensation process[2] described in Table 2. Coating dissipation factors at 350 °C in lab air[3] showed this to be an unsatisfactory coating sol. The sol was deposited by dip-coating (see Section 3.2.2.4).

A2** is a form of A2 reformulated to reduce the precursor condensation rate and give high-density silica films[4].

An A2/A2** stock solution was made by mixing tetraethylorthosilicate (TEOS), ethanol (200 proof), water, and acid (HCl) in a molar ratio of 1:3:1:0.0007 at 60°C in a closed reaction kettle equipped with a stirrer and a cooled reflux condenser. After 1.5 hr. of reaction, the sol was cooled to room temperature and diluted HCl was added to form sols A2 or A2**. The sols were aged as indicated below and then one volume of sol was diluted with two volumes of ethanol to increase the stability of the sol. The sol gave coatings with good quality, homogeneity, and reproducibility when applied by dip-coating.

Al_2O_3-SiO_2 was prepared by separately mixing ethanol-diluted TEOS and HCl solutions and then adding aluminum sec-butoxide[5]. After thorough mixing, the solution was diluted with a large volume of ethanol and refluxed at 80°C overnight. Water was added to give a final molar ratio of water to silicon of 25.

Coating dissipation factors at 350 °C in lab air[3] showed this to be the best coating.

The Al_2O_3-SiO_2 sol is electrophoretically active. Some anodic films were dip-coated with this sol; others were electrophoretically coated (see Section 3.2.2.5). After heat treatment, some of the dip-coated and fired samples were dip-coated again.

7.5S and **20S** are silica sols with water:alkoxide molar ratios of 7.5 and 20, respectively. These sols were made by adding water to the silica stock solution described above. They have been developed as dielectric films for use in the microelectronics industry[6].

The sols were warmed to ~40°C, water (see above) was added, and the mixture stirred 1 hr or until the mixture was fully homogenized. The mixture was cooled to room temperature and one volume of sol was diluted with 2 volumes of ethanol. Both 7.5S and 20S are electrophoretically active and were electrophoretically deposited on anodized substrates.

3.2.2.4 Film deposition by dip-coating.

During dip-coating the substrate is withdrawn vertically from the coating bath at constant speed. A uniform film is deposited on both sides of the substrate; its thickness depends mainly on the withdrawal rate. The dip-coating process is however, influenced by many other factors including solvent surface tension and concentration, differential evaporation of solvents, solution viscosity, and gravitational draining The physics of the dip-coating has been extensively modeled[7].

All dip-coating took place in a glove box under dry nitrogen to preclude hydrolysis of the films by ambient moisture. The film deposition apparatus consisted of a linear motor (resolution = 1,000 steps/mm) and microprocessor controller (Compumotor, manufactured by Parker Hannifin Corp., Petaluma, CA); this allowed precise control of the rate of withdrawal of the sample from the solution. A typical withdrawal rate for the anodized samples was 200 mm/min. Film drying was concurrent with withdrawal. After drying the samples were heat-treated (Section 3.2.2.6).

3.2.2.5 Electrophoresis.

Electrophoresis is movement in solution of charged molecules, particles, or polymers under the action of an applied electric field. During electrophoretic coating deposition, charged particles in liquid suspension migrate toward and deposit on an oppositely charged conductive electrode, which may be either the cathode or the anode depending on particle charge. Electrophoretically deposited coatings have many practical advantages that have led to their commercial use. These include:

(1) many materials can be made electrophoretically active and deposited on conductive substrates,
(2) coating thickness can be readily controlled,
(3) thick coatings (millimeters) can often be applied,
(4) two or more materials can often be co-deposited,
(5) coating occurs rapidly, and
(6) scale-up to production is straightforward.

Deposition rate decreases with time due to the increasing electrical resistance of the growing film during constant voltage electrophoretic deposition. Since film deposition is enhanced in defective regions of the growing film where the electric field is the highest, pin-hole free films of uniform thickness can be deposited on surfaces with complex shapes.

Coatings were electrophoretically deposited by applying a constant D.C. voltage (5V, KH model UHR-220 power supply) between a cathodically-biased anodized substrate and a parallel counter electrode in a glass tank containing the coating sol. Deposition took place in a fume hood to reduce the vapor buildup and explosion hazard. The coating thickness could be varied by changing deposition time (ranged from 5 to 35 minutes). Experiments were performed in lab air.

Samples were withdrawn slowly (25 mm/min) from the sol bath after electrophoretic coating to minimize the thickness of the dip-coated film. Heat-treatment was as for dip-coated samples.

3.2.2.6 Heat treatment.

Coated samples were heat treated in air in a commercial ashing furnace equipped with a microprocessor controller (Fisher Isotemp Model 495, Fisher Scientific, Inc.). No special steps were taken to exclude particles from the heat treatment environment; however, samples which were double coated were blown clean with nitrogen prior to deposition of the second coat. Samples were typically heated at 2°C /min. to 200°C, held at temperature for 2 hr., and cooled at 50°C/min to room temperature.

3.3 Electrical Testing.

Arrays of 6.35 mm diameter, 0.5 micrometer thick gold dots were thermally evaporated onto sample surfaces. The dielectric properties of the coatings were measured across test-capacitor sandwiches with the gold dots and the aluminum substrates as the electrodes. Measurements were made by probing three to five gold dots per sample with a 1.27 mm diameter copper wire electrode bent into a loop. Capacitance, dissipation factor and electrical leakage were measured with a capacitance bridge in lab air (18 to 23°C, 18 to 25 % relative humidity) at 1, 10 and 100 kHz. The breakdown strength was taken to be the voltage at which the leakage current first exceeded 60 microamps (lab air, voltage ramped at 25 V/sec).

4.0 RESULTS.

4.1 Figure of Merit Used to Compare Coatings.

Figure 1 shows that there is little difference between capacitance values measured in lab air and those measured in vacuum (where electrostatic chucks actually operate).for test frequencies from 1 kHz to 100 kHz. Since dielectric measurements in vacuum for the many samples in this study would be are time-consuming and expensive, we measured film dielectric properties in lab air.

Multiplying the 1 kHz sample capacitance by the sample breakdown voltage gives a simple and useful figure of merit for assessing coating properties. This parameter is not expected to depend on sample thickness, a value that is often difficult and time-consuming to measure accurately. The capacitance C of the test samples depends on the permittivity of free space ε_0, dielectric constant κ, capacitor area A and dielectric coating thickness t:

$$C = \kappa\varepsilon_0 A/t.$$

Breakdown voltage V_{bd} depends on breakdown strength and coating thickness:

$$V_{bd} = Bt.$$

Multiplying, we find

$$CV_{bd} = \kappa\varepsilon_0 AB.$$

The product of capacitance and breakdown voltage is the largest electrical charge that can be stored by the capacitor. This figure of merit is useful not only for assessing the quality of a coating, but also for assessing its usefulness in an electrostatic chuck; its square, $(CV_{bd})^2$ is proportional to the maximum chuck clamping force.

4.2 Raw Data.

Figures 2, 3, 4, 5 and 6 show histograms of capacitance-breakdown voltage products for samples produced in a variety of ways. These figures show that the dielectric properties of the composite coatings depend strongly on anodic film porosity, sol-gel coating material, and sol-gel deposition method. Some sol-gel treatments improved coating dielectric properties, while others degraded them.

Figure 2 shows the capacitance-breakdown voltage product for the experimental controls: untreated anodic coatings and anodic coatings sealed with hot water. The best dielectric properties are seen for samples anodized in 10°C electrolyte.

Figure 3 shows the capacitance-breakdown voltage product for 20°C H_2SO_4 anodic films dip-coated with A2 silica sol or with alumina-silica sol. The capacitance-breakdown voltage products for these samples are comparable to those of untreated samples anodized in 10°C H_2SO_4. Sol-gel treated areas of these samples typically have better properties than untreated areas. We hypothesize that the 450°C heat-treatment causes failure of weak areas in the anodic coatings; sol-gel coatings then fill in these areas, leaving the anodic films "better than new". If true, this has important implications for reactor fixturing, electrostatic chucks, and corrosion-resistant coating, where a small number of large defects in protective films can destroy the fitness for service of expensive components.

Figure 4 shows capacitance-breakdown voltage products for anodized samples heat-treated at 450°C before electrophoretic deposition of sols. Sol-gel treated areas typically had better electrical properties than adjacent untreated areas. While results appear to vary substantially with the sol used, the spread in measured values is large. The dielectric properties of a sample anodized at 10°C and then coated with sol 7.5S were better than those of the best untreated anodized coatings. Electrophoretically deposited alumina-silica sols severely degraded the dielectric properties of anodic coatings. This may result from the negative bias applied to the anodic films during electrophoresis; negative bias in reactive media can seriously damage anodic coatings.

Samples anodized in 10°C sulfuric acid and then sealed with a silica sol that produces a high-density coating at low curing temperatures had dielectric properties superior to those of untreated anodic coatings and anodic coatings sealed with hot water (Figure 5).

Anodic films dip-coated twice in an alumina-silica sol gave composite coatings with properties on average better than those of untreated anodic coatings (Figure 6). Comparing the properties of samples that had been dip-coated once (Figure 3) with those that had been dip-coated twice suggests that curing shrinkage may make it difficult to properly seal a porous substrate with a single dip-coating step; additional steps may be beneficial.

4.3 Statistical Analysis.

The dependence of the product of capacitance and breakdown voltage on anodic film preparation and sol-gel surface treatments were evaluated using a commercial statistical analysis software package (JMP Version 2.0.5, SAS Institute) to quantify observed trends. Because of the limited data, we can not say with any certainty that properties of some treated samples are significantly different from those of untreated samples.

Figure 7 shows values of the product of capacitance and breakdown voltage for various surface treatments. Each data point on the graph represents the average value for the three to five dots probed on each sample. Although there are large spreads in values, some trends can be seen. The values for the two samples dip-coated with high-density silica were both high and (desirably) close to each other. Consistency of property values is as important as high values in most applications. Samples dip-coated twice in an alumina-silica sol looks promising for the same reason. One sample electrophoretically coated with 7.5S silica sol had very good properties, but the other as quite poor; the process doesn't seem to be as repeatable as dip-coating with high density silica sol or double dip-coating with alumina-silica sol.

Figure 8 shows a leverage plot with a regression of actual capacitance-breakdown voltage products to means of actual values. The data analysis shows that there is a less than 1 in 8 chance that the observed relationship between post-anodization surface treatments and the product of capacitance and breakdown voltage is the result of random chance. Furthermore, there is a less than 1 in 40 chance that the observed superiority of the high-density silica surface treatment to other surface treatments is the result of random chance.

5. SUMMARY AND CONCLUSIONS.

Sol-gel processing is an important method for producing inorganic coatings when composition, purity, microstructure, process temperature, or manufacturability restrictions preclude fusion or particle sintering. In this study some sol-gel coatings were found to improve the dielectric properties of anodic oxide films, while other sol-gel coatings were found to degrade them. High density silica applied to anodic films by dip-coating using a sol bath gave composite films with the best quality, homogeneity and process reproducibility. Anodic films coated with alumina-silica deposited by double dip-coating or with silica electrophoretically deposited from a low water content sol also had improved properties.

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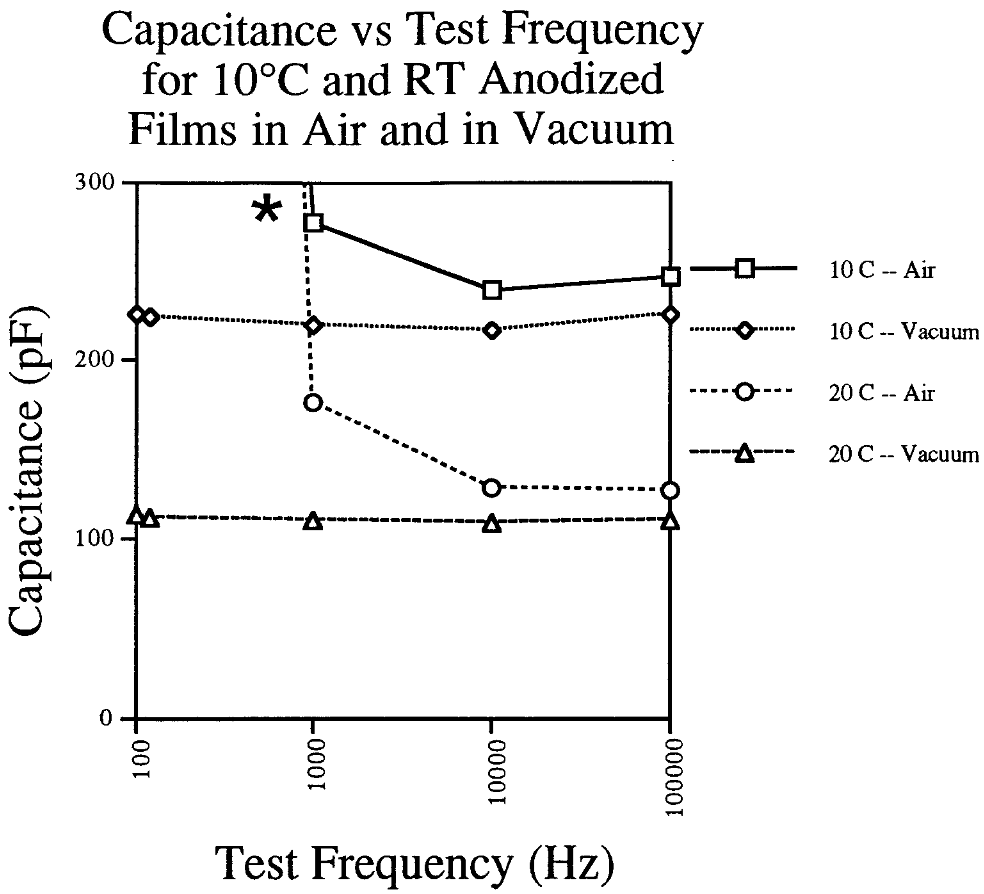


* The capacitance bridge does not accurately measure the capacitance of a lossy dielectric.

Figure 1. Capacitances of 6.35 mm diameter test capacitors on unsealed anodic films (test frequencies - 1 kHz to 100 kHz, test environments - lab air and vacuum).

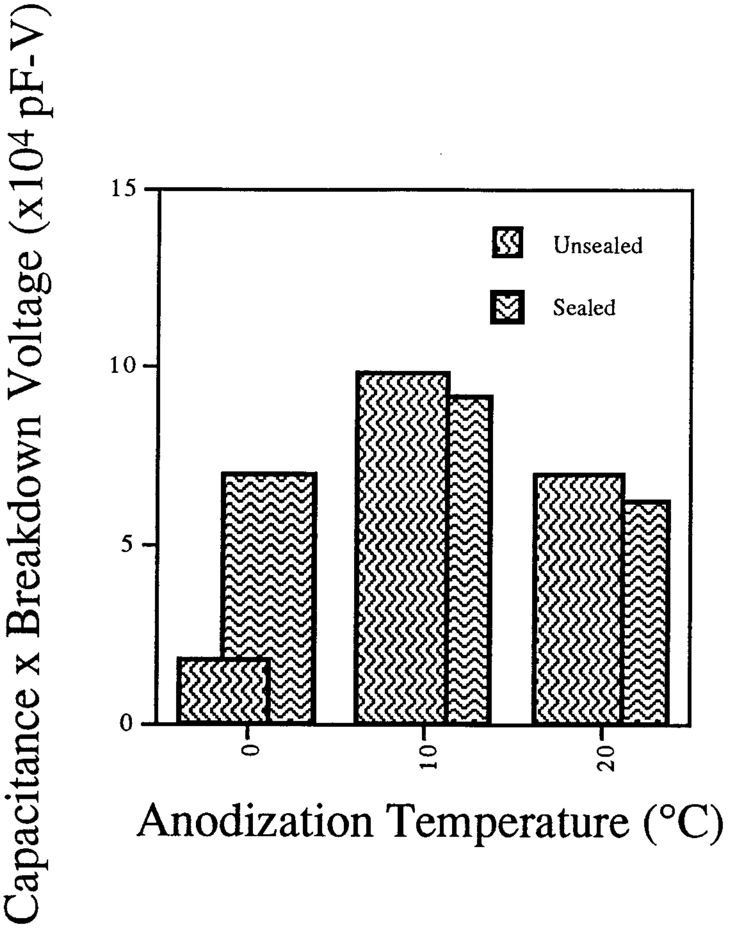


Figure 2. Capacitance-breakdown voltage products for coatings as-anodized and for coatings sealed with deionized water. Best results for samples anodized at 10°C.

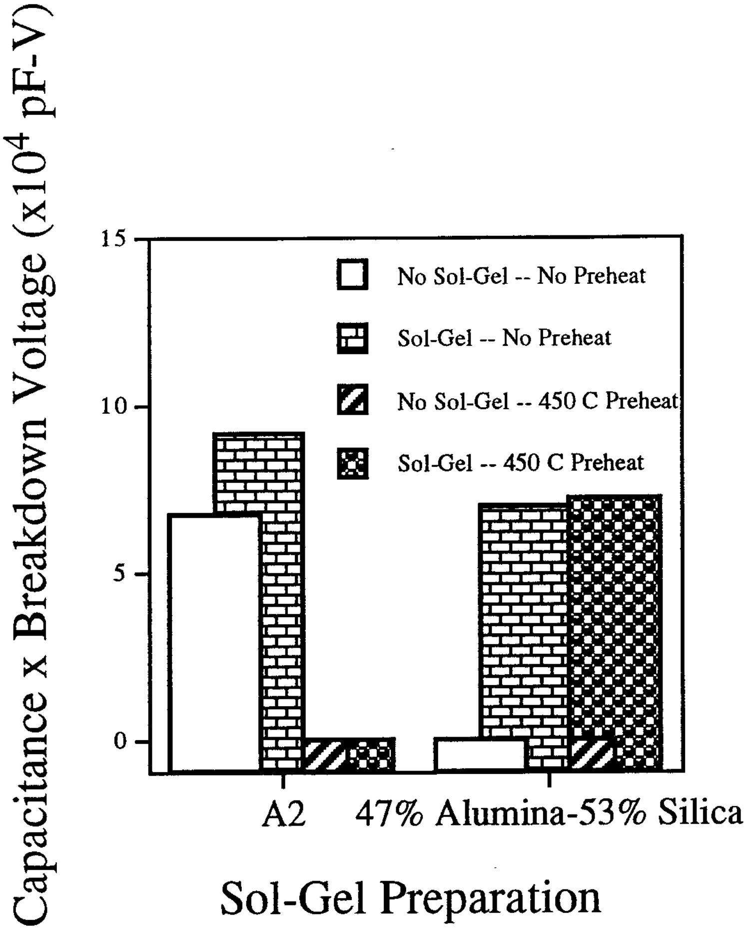


Figure 3. Capacitance-breakdown voltage products for samples anodized in 20°C H_2SO_4 and then dip-coated with A2 silica sol or with alumina-silica sol.

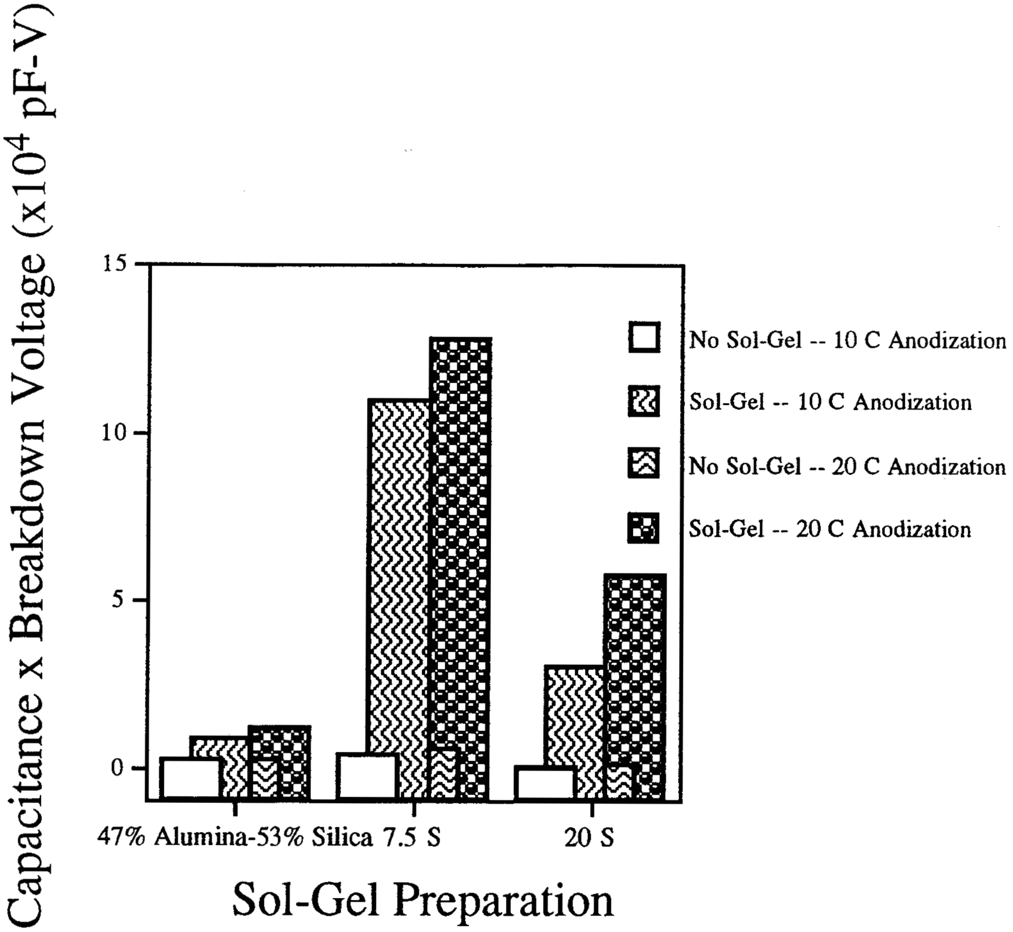


Figure 4. Capacitance-breakdown voltage products for anodized samples that were heated to 450°C before being electrophoretically coated with 20S silica sol, 7.5S silica sol or alumina-silica sol

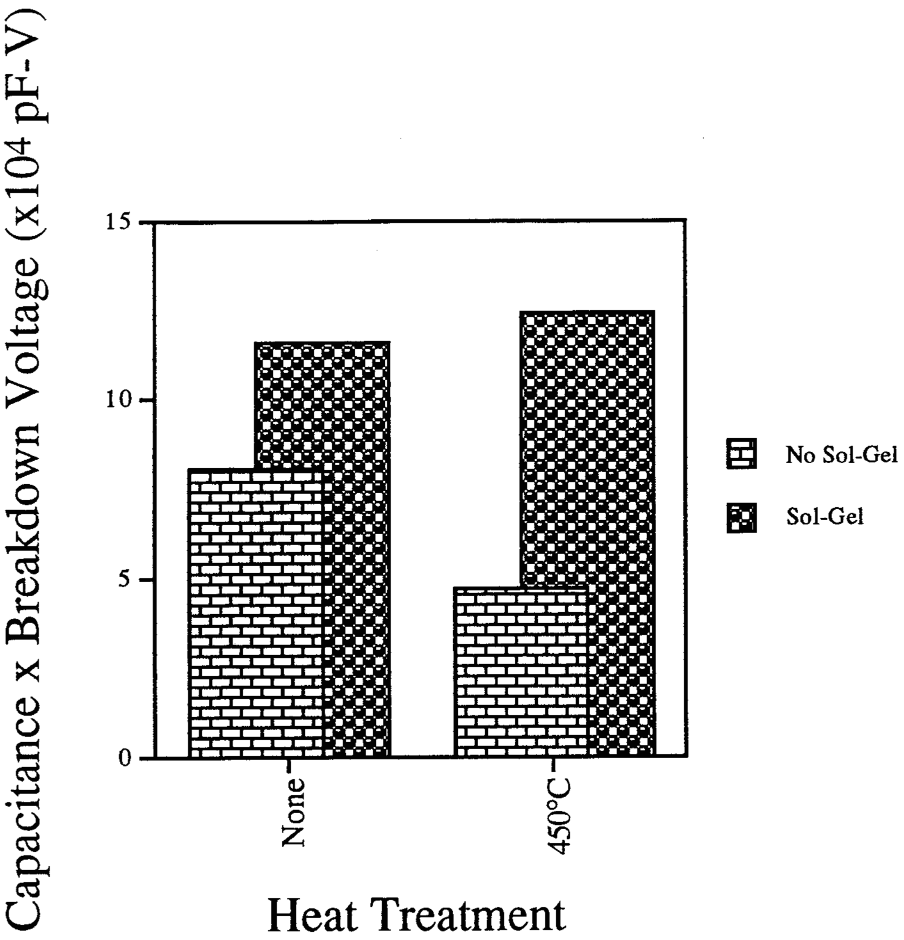


Figure 5. Capacitance-breakdown voltage products for substrates anodized at 10°C and then dip-coated with a silica sol that cures to a high density coating at low temperatures.

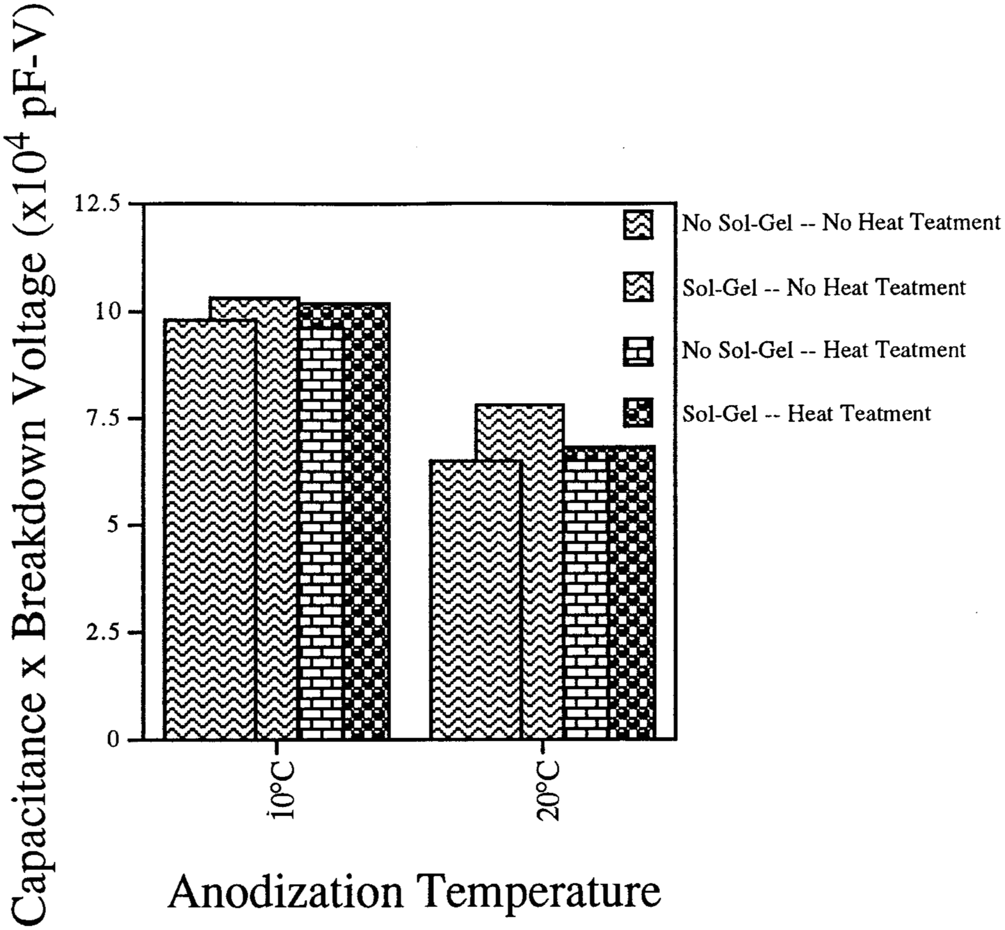


Figure 6. Capacitance-breakdown voltage products for anodic coatings double dip-coated in an alumina-silica sol.

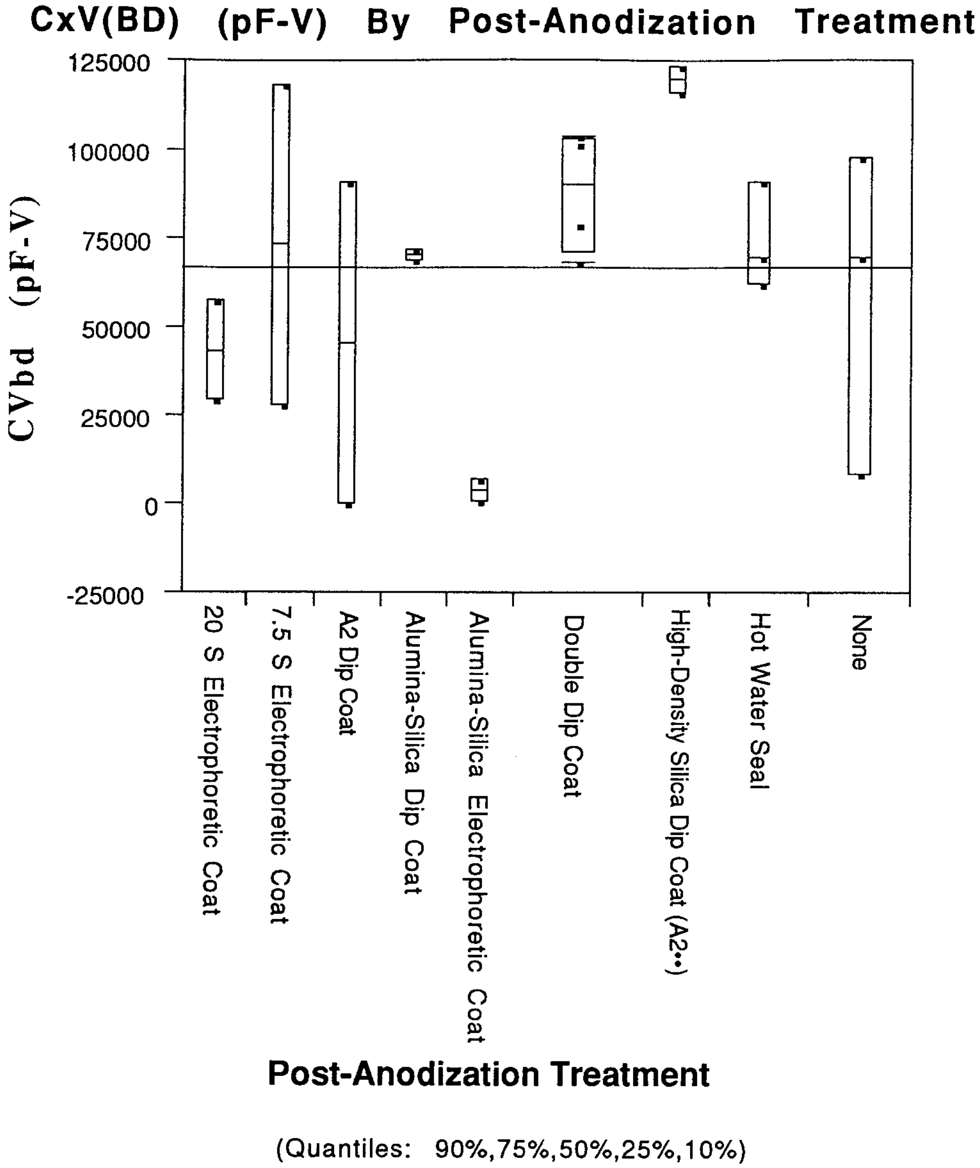
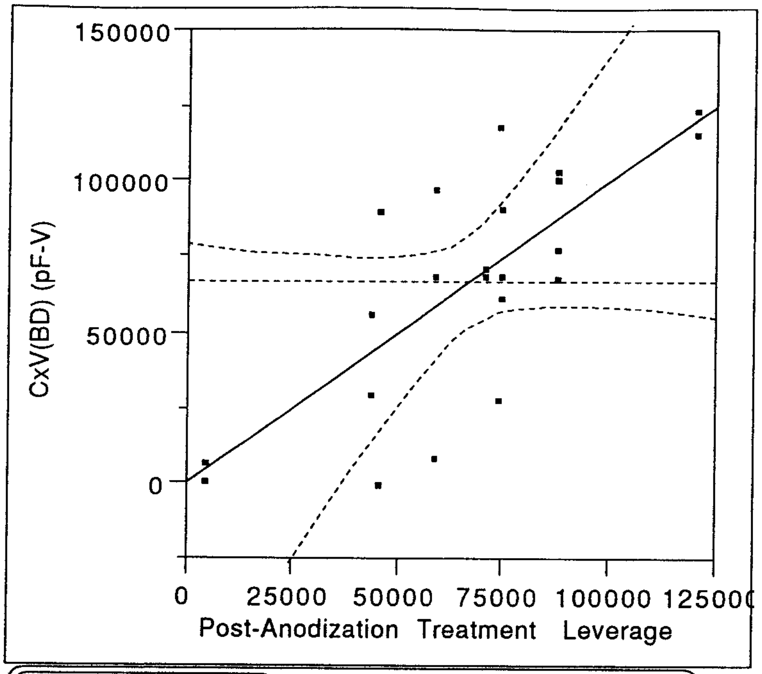


Figure 7. Capacitance-breakdown voltage products for all samples with the indicated sol coatings (90%,75%,50%,25%, and 10% quantiles shown).



Effect Test

Sum of Squares	F Ratio	DF	Prob>F
1.78e+10	2.0518	8	0.1200

Figure 8. Leverage plot showing actual capacitance-breakdown voltage products and regression to means of actual values.

Table 1 -- Process variable choices and surface treatments for samples investigated (surface treatment sols described in Section 3.2.2.3.)

Anodization Temperature	**0°C**	**10°C**		**20°C**	
450°C Preheat?	**No**	**No**	**Yes**	**No**	**Yes**
1. None	2 samples	2 samples		2 samples	
2. Hot Water Seal	2 samples	2 samples		2 samples	
3. A2		2 samples	2 samples	2 samples	2 samples
4. Alumina-Silica		2 samples	2 samples	2 samples	2 samples
5. Electrophoretic Alumina-Silica		2 samples		2 samples	
6. Electrophoretic 7.5 S		2 samples		2 samples	
7. Electrophoretic 20 S		2 samples		2 samples	
8. A2 High Density Silica**		2 samples	2 samples	2 samples	2 samples
9. Double Dip Alumina-Silica		1 sample	1 sample	1 sample	1 sample

Table 2 -- Recipes for A2 and A2** sols.

Preparation of "stock" solution

Reactant	***Volume (ml)***
TEOS	61 ml
Ethanol	61 ml
1M or 0.07M HCl*	0.2 ml
Water	4.87 ml

Stir at 60°C 1.5 hr. with condenser. Store -20°C.

* 1M HCl used for A2, 0.07M HCl used for A2**

To 100 ml aliquot of stock solution, add at ~24°C:

A2	***A2*****
3.9 ml DI H_2O	10.9 ml DI H_2O
12.0 ml 1M HCl	12.8 ml 0.07M HCl

Stir 15 min. at room temperature

A2** sol is "aged" at 50°C for ~16 hr.

Table 3 -- Recipe for Al_2O_3-SiO_2 sol.

	Reactant	***Volume***
Solution 1	TEOS	12.3 ml
	Ethanol	12.3 ml
Solution 2	HCl	2.1 ml
	Ethanol	4.0 ml

Mix solutions 1 and 2 at room temperature

	Al-sec-butoxide	14.2 g
	Ethanol	340 ml

Reflux at 80°C overnight

For 25 H_2O:Si	H_2O	23.1 ml

Table 4 -- Recipes for 7.5S and 20S SiO_2 sols.

Vol. of water for 100 ml aliquot of stock solution

7.5S	***20S***
25.2 ml	72.8 ml