Development of Ultra Clean Photoresist for MEMs Device Applications

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Abstract

Manufacturers of permanent photoresist consider an array of functional requirements when developing new materials. Each step, from synthesis through formulation and film processing, impacts the quality and reliability of the finished product. Typically, pattern-cured formulations consist of functionally different source materials which are employed to match pre-set goals for optical, mechanical, thermal and electrical film properties. However, source materials may contribute ionic and other impurities, either resulting from their respective synthesis, or generated as processing by-products. These impurities can pose a corrosion risk following migration to susceptible metal surfaces with which the film is in contact.

The goal of this work is to identify and understand corrosion risks presented by mobile ion impurities as a function of bulk film thermo-mechanical properties. For permanent films used in inkjet applications, key material properties include glass transition temperature (T_g), modulus and water permeability. Electrochemical Impedance Spectroscopy (EIS) was used along with Dynamic Mechanical Analysis (DMA), to characterize prototype films. The level of corrosive species present was analytically quantified via Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Our data shows that thermo-mechanical properties of fully cured permanent film have significant impact on preventing corrosion with significant amounts of corrosive species present.

Background

High aspect ratio photo-patterned permanent thick film epoxy, such as MicroChem SU-8, has found, and is continuing to find, productive niches in MEMS [1], bioMEMS [2], microfluidics [3], advanced displays [4] and other emerging device technology applications. The patterned epoxy takes form, either as permanent structures in the device, such as display pixel walls, micromachined parts, such as watch gears, or as dielectric layers. As these emerging technologies transition from first proof of concept to large volume production, there is concurrent need for higher reliability, more production-worthy epoxy chemistries. Material specifications for such epoxy materials were, until recently, a problem for MicroChem, as typical epoxy chemistry was considered in the class of UV-Curables and not IC compatible, either in bulk material property or in performance. This problem is gradually being overcome, as Nippon Kayaku, MicroChem's parent company, has become our exclusive supplier of electronic grade epoxy.

In contrast to the transient nature of sacrificial resist films, which are typically removed following substrate etching, the permanent 3D film property of crosslinked epoxy adds yet more levels of material requirement, depending on application. Beyond the nominal physical characteristics defining epoxy chemical structure, such as molecular weight distribution, epoxy equivalent weight (EEW), glass transition temperature (T_g) and modulus, are those desirable bulk electrical characteristics of the crosslinked epoxy network providing galvanic corrosion resistance and dielectric insulation. For the next generation of epoxy permanent films, such electrical properties are needed consistently, formulation lot-to-lot, as part of the material supplier deliverable. Combining these attributes with the high chemical and thermal flow resistance properties of a typical crosslinked epoxy network, makes this class of permanent film becomes an even more viable choice for MEMS and other microelectronic applications.

In 2008, MicroChem introduced a first prototype photo-patterning "corrosion-resistant" material, based on a very low total chlorine bisphenol-A epoxy[6]. Initial successful results in a Highly Accelerated Stress Test (HAST, at 85℃/85% RH/ 1 atm, 96-1000 hr) conditions on Al and Cu surfaces seemed to validate the low total chlorine (<50ppm) approach, but use of more rigorous Pressure Cooker Test (PCT) reliability conditions (120℃/90-100% RH, 2 atm, 24-96 hr) resulted in corrosion test failure. In an effort to understand the cause(s) for such failure, MicroChem and Lexmark International, a leading manufacturer of consumer inkjet printers devices, and a first prototype test partner with MicroChem, joined forces.

Initial EIS testing was conducted at Lexmark on a MicroChem low chlorine "corrosion-resistant" prototype material using a Lexmark-developed epoxy material as an internal standard. Samples were tested in both partially and fully cured states in DI water. Tests showed corrosion developed in the partially cured sample only. This result strongly implied that other variables, beyond low ppm chlorine, were in play. Identification of these variables, the extent to which each variable, and their possible interactions, influences the EIS test result, and the implications of these findings, is the basis for work presented here.

Experimental

In this work, we evaluate two prototype "corrosion-free" resists from MicroChem Corp. EPR-06 and EPR-42 and compared in reference to a Lexmark control. EIS samples were prepared by spinning coating the various resist films onto a Si wafer coated with an AlCu (99.5% Al, 0.5% Cu) metal layer. In the initial round of tests, EPR-06 was tested in both a fully and partially cured states. To achieve a partially cured film, the EPR-06 was

processed through expose, post expose bake (PEB), and develop processes then the wafer was cleaved in half. One half of the wafer was processed through a final hard bake while the second half was left in a partially cured state. EIS testing for round one was conducted in DI water at 60°C.

The second round of EIS testing was designed to examine samples across a range of crosslink densities and molecular weights. To achieve a range of properties, a high molecular weight resist (EPR-42) with a lower EEW was blended with a lower molecular weight resist (EPR-06) with a higher EEW. EIS testing for round two was conducted in a 15ppm chloride solution, also at 60°C. This solution was selected because it is representative of the chloride levels that might be found in an inkjet system. The prototype and blended resists for round two testing are outline in Table 1.

Table 1. Experimental Materials

Resist	Solution	Mw	Cl	X-link ρ
EPR-06	15ppm Cl	Low	Low	Low
3:1 blend	15ppm Cl	Med	Low	Low
1:1 blend	15ppm Cl	Med	Med	Med
1:3 blend	15ppm Cl	Med	Med	High
EPR-42	15ppm Cl	Med	Med	Highest
LXK Control	15ppm Cl	High	High	Med

Materials

The prototype EPR-06 features specially treated low total chlorine, high EEW (lower crosslink density) bisphenol-A epoxy. Prototype EPR-42 employs an experimental, higher total chlorine, low EEW epoxidized bisphenol-A novolac. Both incorporate an *i*-line sensitive onium salt photoacid generator (PAG), some appropriate film additives containing essentially no significant mobile halide, and a casting solvent. The two prototypes and three blends resulting from combination of each prototype, as well as the respective experimental levels of three representative variables in the formulation space, are shown in Table 1. It was desirable that the physical properties for both the single component prototypes and the three blended resists would provide wide enough material variability to effect the EIS response.

The Lexmark control resist is comprised of three different resins. The first component is a high molecular weight, low EEW epoxy resin, the second a high molecular weight, high EEW phenoxy, and the third a low molecular weight, low EEW naphthalene resin. The resins are blended with a casting solvent and i-line sensitive PAG (onium salt) along with additional additives to achieve the desired film performance. In contrast to the MicroChem prototype resins, the resins used in the control formulation were not treated or processed to produce ultra-low Cl ion levels and so provided an ideal control.

EIS Testing

The experimental foundation for this work involves Electrochemical Impedance Spectroscopy (EIS). The EIS flat cells were connected to a Princeton Applied Research Model 273A potentiostat, a Solartron model 1281B multiplexer and Solartron model 1255B frequency analyzer. The CorrWare and ZPlot v.3.2b EIS software and control instrumentation used was from Scribner Associates Inc. In this set of EIS experiments, prototype epoxy-based photoresists were coated over an AlCu (99.5%Al/0.5%Cu) surface then immersed in an electrolyte solution. A low amplitude AC signal was then applied to the EIS test cell (Figure 1) and the signal ramped from 60kHz to 0.1Hz in 10 steps per decade. The electrical impedance and open circuit potential vs. an Ag/AgCl reference electrode of the system was monitored over two weeks. The pore resistance, R_{pore}, which is a measure of the ionic conducting path through the epoxy coating and the in-tact coating capacitance, C_{coat}, were then extracted from the EIS data (Nyquist and Bode plots). The presence of a Warburg element, which is indicative of a diffusion process, allows the diffusion coefficient for chloride through the epoxy coating to be extracted from the EIS test data. A more detailed explanation of EIS test theory can be found elsewhere in the literature [6].

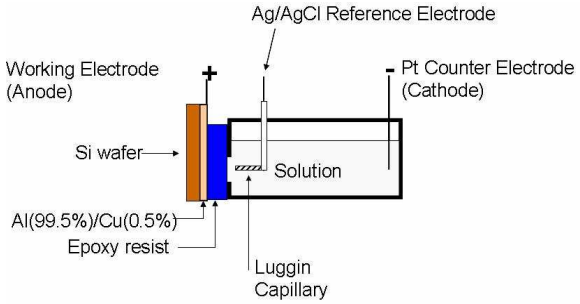

Figure 1. EIS Flat Cell

Thermo-mechanical and Chemical Analysis

In order to better understand the EIS test performance of the prototype materials, the thermo-mechanical and chemical properties of each resist were fully characterized. The Glass Transition Temperature (Tg) and crosslink density were evaluated by dynamic mechanical analysis using a Q800 Dynamic Mechanical Analyzer by TA Instruments. Fully cured free standing films approximately 50um in thickness were ramped from -50°C to 300°C with a ramp rate of 3°C/min and frequency of 10Hz.

For each prototype resist the molecular weight (Mw) was determined by Gel Permeation Chromatography (GPC), and the Epoxy Equivalent Weight (EEW) was measured by titration. Additionally, the total and extractible level of chloride ions were measured by Ion Chromatography (Dionex-600) of bomb combusted and water extracted samples respectively. Lastly, the mobile cations were quantified by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Results and Discussion

As mentioned, the impetus for using these two epoxy components derived from the need for wide variability of the bulk physical properties (Total Chlorine, Mobile Chloride, EEW, etc.) in the test space. Further, blending of the two formulated components did provide continuous variability in physical properties (Table 2) and in EIS response (Table 3). These formulation prototypes are not commercially worthy as engineered products, as they are not designed for any particular field application, but rather are composed for the experimental work

presented herein. That said, the learning shown here will assist in development of future generations of photo-patterning epoxy products.

Table 2. Analytical Results Summary

Resist	Tot. Cl, ppm	Mobile Cl, ppm	EEW	X-link ρ	M_w	T_g, C
-06	12.9	1.85	*543*	16	4831	120
3:1	67.2	<LOQ	715	19	5398	162
1:1	128	4.98	493	50	5557	204
1:3	198	<LOQ	341	65	5756	260
-42	228	na	*195*	423	5887	290
Control	773	1.15	588	55	8710	168

As expected, the two prototypes and three blends generally show a wide, continuous range in Mw, Tg, and EEW. The EEW values reported for EPR-06 and EPR-42 are calculated values based on their single epoxy chemistries, while the EEW values for the blended samples were measured by titration. Thus there is a discontinuity with respect to the EEW for EPR-06. Crosslink density values derived from DMA testing continuously increased with increasing proportion of EPR-42. Interestingly, the Lexmark standard shows a range of values matching some of the individual properties of the prototypes while not matching any one prototype. In particular, the crosslink density of the Lexmark control is most similar to that of the 1:1 blended prototype, while the molecular weight is significantly greater than any of the MicroChem prototypes.

Table 3. EIS Results Summary

Resist	ε	Δ C_{coat}, F	R_{pore}, Ω	D, m^2/s	Corrosion
DI Water					
-06, Cured	8.68	--		9.6E-23	No
-06, Partial cure	14.8	--		1.1E-20	Yes
15ppm NaCl Solution					
-06	5.27	2.3E-06	1.0E+05	Na	No
3:1	7.84	1.7E-09	2.3E+08	1.1E-20	Unclear
1:1	6.04	4.6E-10	9.2E+08	2.6E-22	Yes
1:3	5.95	4.9E-10	7.4E+08	5.0E-22	Yes
-42	7.41	6.5E-10	4.4E+09	2.1E-22	Yes
Control	6.51	5.1E-10	1.2E+09	3.8E-22	No

Consider from Table 2 the first two variables total chlorine and mobile chloride. EPR-06 shows both the lowest total chlorine and lowest mobile chloride of the samples tested. The initial hypothesis for formulation of prototype EPR-06 postulates low total chlorine will decrease the chances for generating additional mobile chloride through further conversion of halohydrin (consequence of incomplete epoxidation reaction), either in the liquid formulation, or in the processed hardened film. The expectation is to not observe any significant EIS response, if both total chlorine and mobile chloride are nominally low. Referring to Table 3, the EIS response for totally cured EPR-06, in DI water, showed no visual corrosion response, while the partially cured sample did. For EPR-06 exposed to a 15ppm NaCl solution, conditions similar to the other prototypes and the standard, the visual corrosion test was inconclusive, while EPR-42 and standard showed no visual corrosion. These examples illustrate that variables other than total chlorine and mobile chloride play a role in corrosion resistance.

Crosslink density, molecular weight and T_g all show general correlation to the EIS measured values for pore resistance (R_{pore}). Figure 2 (Pore Resistance vs. Test Time) shows two distinct sample responses occurring over the t=0 to t=2 day time period. For the EPR-06 prototype, a precipitous five order of magnitude drop in pore resistance is observed after 48 hours; thereafter, the sample shows steady behavior for the remainder of the test period.

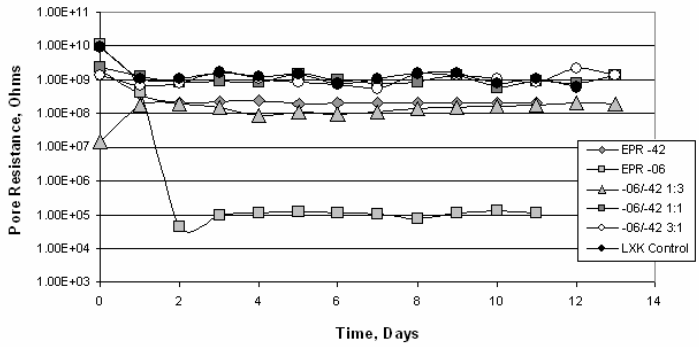

Figure 2. EIS Results for Pore Resistance

The remaining samples, save one, show only a nominal drop-off (1-2 orders of magnitude) after one day to steady pore resistance through the remainder of the test period. The large magnitude drop-off in pore resistance for EPR-06 may be due to either of two phenomena: (1) a defect in the epoxy film and/or Al/Cu substrate, which caused an unexpected acceleration in degradation, or (2) a large uptake of water in the film, which caused acceleration of ion mobility, as shown by a loss of pore resistance. The gravimetric measurements taken for fully cured, free standing films soaked at 70°C showed the mass uptake in DI water ranged from 1.8% - 2.5%. This suggests that the EPR-06 test specimen was likely damaged or defective at the start of testing.

The remaining samples show only a modest decline in R_{pore} from T_0 throughout the test period indicating a modest uptake of water. But, within the other prototypes and the standard, no clear distinctions are seen. However, the measured crosslink density of EPR-42 is clearly an outlier relative to the other samples and the control. A trend of increased stress was evident in the surface cracking observed in the EPR-42 and 1:3 (-06:-42) blended samples relative to the other samples, where little or no surface cracking was evident. Also of note are the EIS results for EPR-42's dielectric constant, C_{coat} and R_{pore} values (Table 3). These values place EPR-42 in the low-to-middle response range, which allows for prediction of corrosion. However, in the case of EPR-42, the ultra-high crosslink density appears to overwhelm all other physical characteristics used as metrics for this corrosion study. Indeed, visual inspection of EPR-42 showed no corrosion. While neither the EPR-42 nor Lexmark control samples showed a signal for corrosion in EIS testing, visual inspection of the Lexmark

control did show a few areas of minor film delamination which may indicate the beginnings of a dielectric double layer forming between the film and metal interface. Surprisingly, all three blended samples produced metal film pitting and/or epoxy film delamination in the EIS tests, though no clear trend was observed with respect to physical film properties.

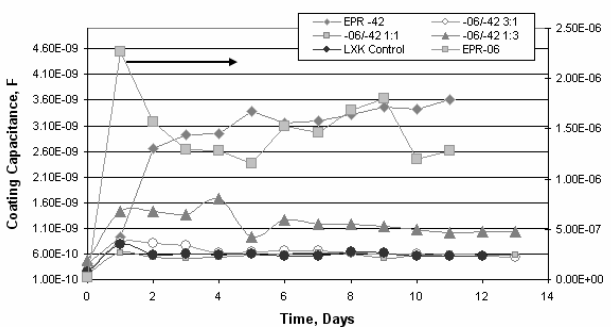

Figure 3. EIS Results for Coating Capacitance

The coating capacitance, C_{coat}, as a function of time, is shown in Figure 3. An initial increase in capacitance is seen over the course of the first 24hrs as water is absorbed into the coatings. Then, because capacitance is inversely related to thickness, the C_{coat} values decline to a steady state as the coating increases in thickness due to swelling. Here a trend of increasing capacitance with increasing parts EPR-42 is observed for the EPR-42 and the 1:3 blended (-06:-42) samples. The EPR-42 shows nearly an order of magnitude difference compared to the other blended samples and the Lexmark control. This difference could be explained by the high density of EPR-42 surface cracks (high crosslink density) contributing to increased surface area for this coating, and a net increase in swelling. Since no corrosion was seen for EPR-42, the swelling difference may be limited to the outer most surface.

Nearly all EIS test cells showed the presence of a Warburg diffusion element (evidenced by a 45° line on the EIS Nyquist plot) which allowed the coefficient of diffusion to be calculated for Cl ions through the thin film coatings. Diffusion coefficient values for the sample resists ranged from 10^{-20} to 10^{-22} m^2/sec. From Fick's first law, the diffusion coefficient for water in an epoxy system is on the order of $10^{-12}m^2$/sec which is eight to ten orders of magnitude faster than the values calculated for the resists tested. This is consistent with previously reported values of 10^{-17}-10^{-18} m^2/sec for Cl ion diffusion through a low crosslink density epoxy adhesive [6]. Others have reported Cl ion diffusion to be on the approximately 9 orders of magnitude less than that of water as measured by DSIMS [7].

Summary/Conclusion

We have presented evidence that ultra-clean resists for MEMS applications can be produced for use in applications requiring minimal galvanic corrosion. Some conclusions follow:

1. EIS provides significant insights into the mechanisms governing galvanic corrosion.
2. High crosslink density may well play a dominant role in producing overwhelming resistance to an electrolyte at the epoxy film surface, as well as drastically slowing ion diffusion in the EIS stack.
3. Reducing total chlorine had no impact on EIS results reported here.
4. Mobile chloride is implicated in galvanic corrosion, but its effects can be mitigated by control of film properties, primarily that of crosslink density.
5. Factors other than high crosslink density play a lesser, but still significant role, in preventing ion migration in epoxy films.
6. Epoxy surface swelling resulting from contact with water may be enhanced by high film stress surface cracks, which may inhibit, or prevent, water and ion migration, relative to less stressed films.
7. EIS results from this work hint at the roles which chemical and film crosslink architecture play in minimizing water and ion migration.
8. Further correlation of EIS to other reliability testing, such as HAST and PCT, is necessary.

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Author Biography

Dr. George Cernigliaro, Vice President and CTO of MicroChem Corp, is leading technical efforts to develop next generation material and process platforms for MEMS, BioMEMS and microelectronics applications. He was a Principle co-founder of Advanced Nanotechnologies, Inc, a start-up focused on consulting and development of fully functionalized permanent films for high technology applications. A classically trained organic chemist, he has held a wide variety of technical and R&D management positions over a long, successful career.