

Maximizing Selectivity During Wet-Chemical Gold Etching

K.C. Su,^a H.H. Lu,^a C.C. Chen,^a and J.C. Moore^b

^aLee Chang Yung Electronic Materials (LCYEM), 4F, No. 83, Sec. 4, Bade Road, Taipei, 105, Taiwan R.O.C.

^bDAETEC, LLC, 1227 Flynn Rd., Unit 310, Camarillo, CA 93012, USA

^a886 (2) 2763-1611, e-tech@lcy.com.tw, ^b(805) 484-5546, www.daetec.com

Keywords: Au bumping, UBM, etch rate, inhibitor, iodine/iodide.

Abstract

Gold metallization is well known for its preferred properties of conductivity and corrosion resistance in GaAs wafer manufacturing for patterned metal lines and backside thermal sinks [1-3]. In flip-chip processing, electroplated gold bumps are used to establish the main input/output (I/O) terminals between chip and board contact [4-5]. During manufacturing, it becomes necessary to remove unwanted thin seed layers of gold in order to isolate the feature and adjacent insulation. Etching is normally conducted with a chemical mixture of iodide and iodine along with additives, which aid in processing. These mixtures are known to be aggressive to other metals such as aluminum. Chemistries have been developed which protect these metals. Typical etch rates for gold in such solutions are approach 5000Å/min and provide a poor selectivity ratio of $\leq 20:1$. Inhibited systems can improve selectivity by more than 100-fold. Further discussion of the gold tech chemistry variants, inhibitors, and processing results are discussed.

INTRODUCTION

Gold metallization is applied as an electrical contact layer in GaAs LED chips and bumping. Gold bumping technology, designed to replace wire bonds, is applied on TCP (Tape Carrier Package), COG (Chip on Glass), and COF (Chip on Film) primarily for LCD driver ICs. The bump is produced by a range of practices to include ECD (electrochemical deposition) during WLP (wafer level packaging). Most bump processes are done on 150mm or 200mm wafers. Gold bumping provides the best solution for fine pitch features near 10~30µm and where low packaging profiles are needed. WLP processes allow many feature designs to be made for high volume LCD driver ICs (Figure 1).

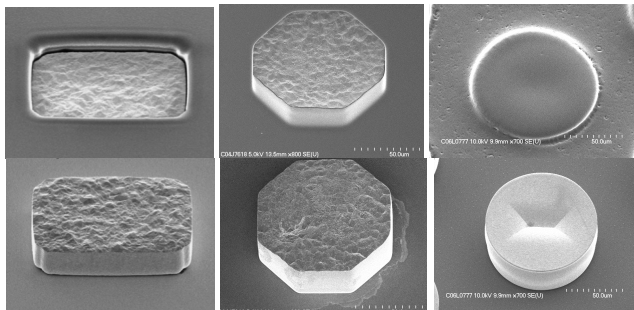


Figure 1. SEM photos of various gold bumps with thick resist (above) and stripped with LCYEM products (below).

As requirements increase with high I/O, flexible interconnects, thin substrates, and lightweight packages, gold

bumping is becoming the method of choice in WLP to achieve these objectives. Features approaching 100µm may be produced in high volume and be cost effective with WLP practices using thick resists and chemical strippers, such as the ST-5000 series produced by LCYEM [6].

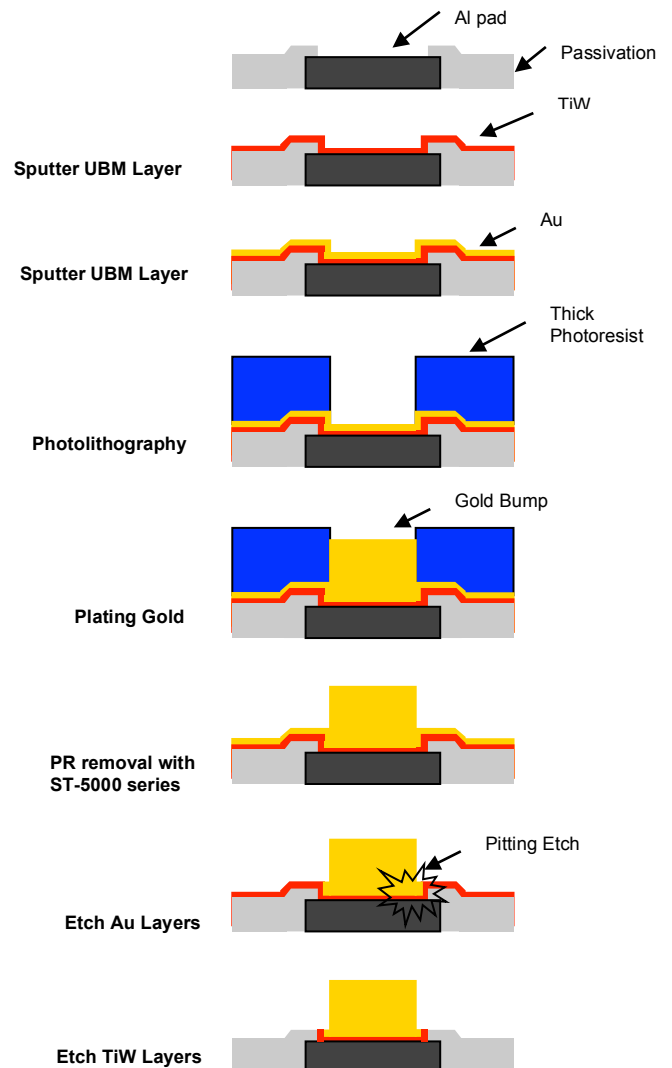


Figure 2. Example gold bump process flow, showing opportunity for metal etch during chemical exposure.

As indicated in figure 2, gold bumps are electroplated on a sputter UBM layer. Several different metallization schemes

are used as UBM, however, most involve some amount of gold (Au) with other noble metals. Example UBM layers include: TiW/Au, TiWN/TiW/Au and Cr/Ni/Au [7-8]. In these cases, thickness varies between 500-3000 Å, with TiW or Cr/Ni representing a minor component. During UBM etch, process variation can cause the Al pad to be compromised, resulting in pitting, undercutting, and related galvanic corrosion.

Although several approaches may be available, the use of wet etching processes are the most economical, substrate passivation safe, and easiest to integrate. The etching of gold may be done with aqua regia, a mixture of hydrochloric and nitric acids (HCl:HNO₃, 3:1), however, this solution is not stable. Etch rates in aqua regia may exceed 1 µm/min with little or no selectivity over Al, or for that matter, any other metals. A common alternative is the use of aqueous iodide-iodine, where Au etching may be 0.1 µm/min while Al loss can be <0.01 µm/min. Selectivity is typically 10-20:1 for Au:Al at room temperature. Unfortunately, this level of selectivity may not be enough for many devices. End-users demand Au etchants to be inhibited towards Al and related metals without compromise to Au etch performance.

EXPERIMENTAL

Several inhibitors were chosen to achieve selective etching of gold. Although many materials are known for aluminum protection, they are in limited use based upon their low solubility in high salt mixtures. For example, aluminosilicates are well known for chemisorption protective coatings [9], however, silicates are pH sensitive with preferred solubility in alkalis. Benzotriazole (BTA) is selective for Cu and preferred in neutral pH. Solution extremes may use tolyltriazole (TTA) or related derivatives to improve surface passivation [10-11], however, both BTA and TTA exhibit low aqueous solubility. For these reasons, this investigation focused on simple inorganic or highly aqueous soluble reagents known to exhibit surface activity (Figure 3).

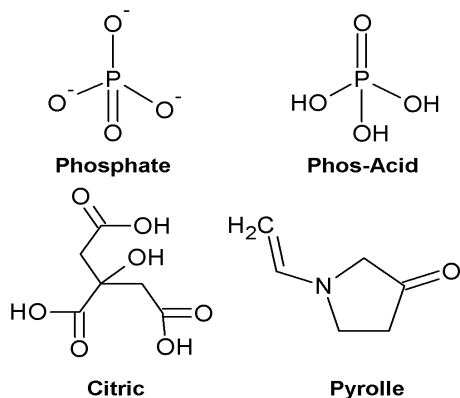


Figure 3. Aluminum inhibitors investigated for Au etchant.

The inhibitors chosen for this investigation included phosphates, citrates, and highly aqueous pyrrole polymers, similar to Aq_PCoatTM as developed by LCYEM for water-

wash coatings during laser processing [12]. Stock Au etchant is prepared to a molar ratio I₂:I⁻ as approximately 1:10, or 0.016M and 0.17M for I₂ and I⁻, respectively. Inhibitors were screened for solubility @ 5% (w/w) in the stock solution. Aqueous polymers are chosen for stability based upon molecular weight, functionality, and the affects on the colligative properties of the solution.

Table 1. Solution stability of inhibitors in Au stock solution.

Chemistry	Stability
Phosphate acid	Clear
Citrate	Clear
Phosphate	Clear
Pyrrole	variable

Etch rate is determined by gravimetric analysis using pure Al & Au foil, conducted at room temperature to model the gold bump process. Analytical equipment beyond the use of normal ware expected in a chemistry/apps lab includes SEM (Hitachi 4700) and sample preparation tools.

RESULTS

Like many chemical processes, typical Au etch solutions are governed by chemical, temperature, agitation, and the device design. Iodine (I₂) dissolves slightly in water, giving brown solutions. Iodide (I⁻) dissolves iodine readily giving deep purple solutions. Iodine and iodide combine reversibly to form the complex ion I₃⁻, shown in reactions (1-2):



Etching of Au is due to the reduction of I₂ and I₃⁻ in the presence of I⁻. Acidic conditions support the reduction of dissolved oxygen and formation of the AuI₂⁻ complex. These factors and the high activities of iodine species contribute to spontaneous Au etching. Metallic I₂ is mixed with I⁻ to achieve a desired etch rate (Figure 4).

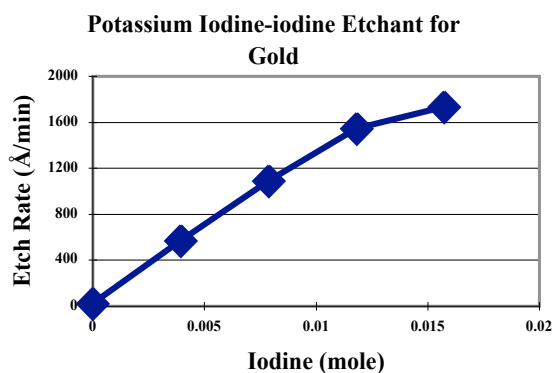


Figure 4. Iodine bath preparation is designed to meet a desired rate.

Etch rate selectivity is determined for Au over Al, presented in Table 2 and the averages graphed in Figure 5. The inhibitors shown in Figure 3 and Table 1 are tested over a concentration range to 7.5% in stock Au etchant. It is desirable to achieve a high selectivity without significant reduction in Au etch performance.

Table 2. Etching rate and selectivity for Au and Al.

Chemistry	Inhibitor (wt%)	Au Etch rate (Å/min)	Al Etch rate (Å/min)	Au:Al Etch Selectivity
Reference	0	1200	70	17:1
Phosphate acid	2%	819	24	34:1
	5%	891	34	26:1
	7.5%	829	34	24:1
Citrate	2%	933	24	39:1
	5%	780	24	32:1
	7.5%	840	24	35:1
Phosphate	2%	840	14	61:1
	5%	840	10	82:1
	7.5%	840	3	245:1
Pyrolle	1%	663	21	32:1
	7.5%	210	3	70:1

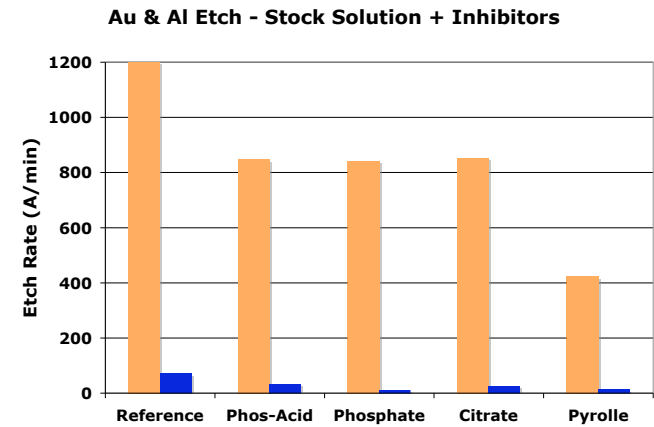


Figure 5. Au and Al etch selectivity as described in Table 2.

Reference and inhibited Au etch solutions were tested on device aluminum pads at RT 30min. Specimens were observed for attack by optical (OM) and SEM (Figures 6-7).

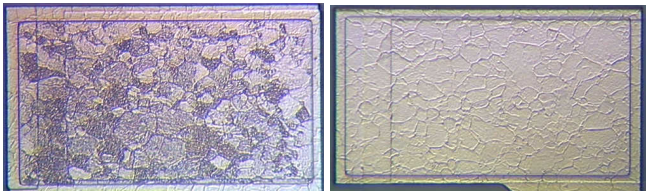


Figure 6. OM photos of device Al pads, reference (left) and inhibited (right).

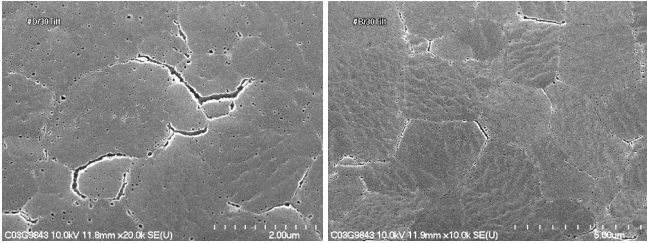


Figure 7. SEMs of Al pads (Fig.6), reference (left) and inhibited (right).

The photos of device aluminum pads suggest serious attack by the reference solution (no inhibitor), resulting in exposure of the Al metal grains (e.g. blackening) in the OM photo (Fig. 6, left) and etch at the grain boundaries (Fig. 7, left). The same Al pads and respective microscopic metal regions of the inhibited solution appears to be intact.

DISCUSSION

The etch selectivity of Au over Al can be discussed by considering many influences. Certainly, Al exhibits a higher oxidation potential (i.e. $\text{Al}_{(s)} \rightarrow \text{Al}^{+3} + 3\text{e}^-$ $E^0 = +1.66\text{V}$) than Au metal (i.e. $\text{Au}_{(s)} \rightarrow \text{Au}^{+3} + 3\text{e}^-$ $E^0 = -1.42\text{V}$), however, we have already mentioned that several redox and complexing reactions contribute to Au etching.

The benefits of certain inhibitors for Al have been shown, however, some materials may reduce the activity for both Au and Al. The inhibitors noted to be best are phosphate and citrate derivatives. Their average selectivity varies as 30-90:1 for Au:Al. Based upon experience in the fab, the customer target is near 50:1. LCYEM has investigated this area and produced several options to produce high selectivity solutions for Au over Al at >50:1. These materials are being supplied into the gold bump and related businesses.

Recycling of waste Au etchant is provided by industries supporting the recovery of precious metals. Typically, a reducing agent is added with a buffer to cause precipitation of the metal. The spent solution is then treated by oxidization or further precipitation to drive species to their baseline, which may be used as components for a new etching solution [13].

CONCLUSION

Several inhibitors have been identified and characterized for improved Au etch selectivity to be used in gold bump or similar processes. These inhibitors include phosphate and citrate derivatives and an aqueous soluble pyrolle polymer representative. Etch selectivity was measured at greater than 90:1 as compared to a reference of 17:1, for Au:Al. An Au etch selectivity of >50:1 is desirable. Tests on Al pads show protection with reduced metal grain attack as observed by SEM. Several options exist to achieve this target based upon LCYEM's commercially available products.

ACKNOWLEDGEMENTS

The authors would like to thank the staff at LCYEM, Daetec, and Mr. Han-Wei Shen of Evans Analytical Group for their support in making this work possible.

REFERENCES

- [1] H. Hendriks, A. Hanson, T. Lepkowski, A. Quaglietta, and B. Patel, "Benefits and Challenges in Decreasing GaAs Substrate via Size and Die Thickness", GaAs ManTech Conference, pp. 105-108, **(2002)**.
- [2] H. Hendriks, J. Tajadod, and J. Klocke, "Photoresist Application for 3D Features on Wafer Surfaces," *Compound Semiconductor*, June, **(2003)**.
- [3] J. Moore, S. Luna, T. Rivers, B. Howell, and C. Becker, "Removal of Gold Impregnated Etch Residue from Front and Backside Vias in a Single Process," GaAs ManTech Conference, pp. 273-276, **(2005)**.
- [4] D. Evans, "Gold Bump Technologies Plating versus Ball", Internet Micro. ad Pkg. Sac., No. MP22, March, **(2005)**.
- [5] C-Y. Liu, S-J. Wang, "Gold Bump Structure and Fabrication Methods Thereof", U.S. Patent No. 20,030,019,481.
- [6] K.C. Su, C.C. Chen, Y.C. Chen, and J. Moore, "Cost Effective Inhibitors Used for FPD Device Protection During Polymer Stripping Processes," Asia Display conference, **(2007)**.
- [7] US Patent No. 4,927,505, R. Sharma, H. Geyer, and D. Mitchell, "Metallization Scheme Providing Adhesion and Barrier Properties."
- [8] US Patent No. 5,310,699, Y. Chikawa, S. Sasaki, K. Mori, T. Maeda, M. Hayakawa, "Method of Manufacturing a Bump Electrode."
- [9] J.P. Labbe, and J. Pagetti, "Study of an Inhibiting Aluminosilicate Interface by Infrared Reflection Spectroscopy," *Thin Solid Films* 82:1, 113-119, **(1981)**.
- [10] J. Moore, I. Lorkovic, and B. Gordon, "Rapid Methods of Characterizing Triazole Inhibitors for Copper and Cobalt Processes," CMP Users Group, AVS Society, October, **(2005)**.
- [11] J. Marsh, R. Pearson, B. Strickland, J. Moore, and S. Raghavan, "A Review of Semiconductor Manufacturing Applications Using Triazole-Based Inhibitors for Copper and Related Metals," Semiconductor Processing with Wet Chemicals Conference (SPWCC), February **(2005)**.
- [12] K.C. Su, H.H. Lu, S.H. Chen, C.D. Tsai, Y.C. Chou, b W.J. Wu, G.Q. Wu, and J.C. Moore, "A Novel Water-Washable Coating for Avoiding Contamination During Dry Laser Dicing Operations", GaAs ManTech Conference, **(2007)**.
- [13] US Patent No. 5,137,700, H. Sloan, "Processes Employing Iodine-iodide Etching Solutions."