Improvements in the Process for Electrodeposition of Au-Sn Alloys

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Abstract

An electroplating process has been developed to deposit gold rich, Au-Sn eutectic alloys from a single, non-cyanide, slightly acidic bath onto metallized semiconductor substrates. However, commercial exploitation is limited by plating bath lifetime and plating rates. In this paper, the most effective factors influencing the lifetime and the plating rate are determined. Next, a statistical design approach (Box-Behnken) is taken to try to optimize the essential factors and, consequently, electrolyte lifetime and deposition rates. A multiple response optimizer using commercial software can then be used to analyze the data to determine the optimal combination of solution components to both improve the stability and the plating rate.

INTRODUCTION

Gold-tin eutectic solders have been widely used in the optoelectronics and microelectronics industry for packaging applications. An electroplating process has been developed to deposit Au-Sn alloys from a single, non-cyanide, slightly acidic bath onto metallized semiconductor substrates. The bath constituents and their nominal functions are summarized in Table I [1]. A combination of multi-layered phases Au_5Sn and AuSn can be used to produce an artificial eutectic structure. This solder is well-known for its high thermal fatigue resistance in addition to excellent thermal properties. However, the lifetime of the bath solution is limited to two-three days due to gold precipitation [2]. Moreover, the plating rates are fairly low [2].

TABLE I
AU-SN PLATING SOLUTION CONSTITUENTS AND FUNCTIONS

Chemical	Function
$KAuCl_4$	Au^{3+}
$SnCl_2.2H_2O$	Sn^{2+}
ammonium citrate	Buffer
sodium sulphite	complexing agent
L-ascorbic acid	prevents Sn hydrolysis

In any experiment, one or more process variables (or factors) are intentionally changed in order to observe the effect the changes have on one or more response variables. One efficient procedure for planning experiments is the statistical design of experiments (DOE). These experiments are designed so that the data obtained can be analyzed to yield valid and objective conclusions [3].

Any process can be modeled in the form of a `black box', with several discrete or continuous input factors that can be controlled and varied intentionally with one or more measured output responses (Figure I). The output responses are assumed to be continuous. Then, the obtained experimental data are used to derive a practical approximation model linking the outputs and inputs [3].

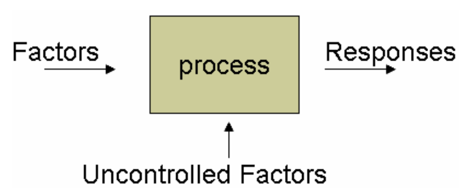


FIGURE I: BLACK-BOX MODEL

The objective of these experiments is to select the key factors affecting the stability and the plating rate, and to find improved and optimal process settings.

SCREENING TESTS

The most effective factors influencing the lifetime and the plating rate were determined using screening tests. Transmission electron microscopy (TEM) analysis was done to monitor gold precipitation during the mixing procedure. When ammonium citrate and $KAuCl_4$ are mixed, gold precipitation occurs early in the mixing process (Figure II). Since gold precipitation is observed as a result of aging of the solution, the concentration of ammonium citrate in the solution was believed to be an important factor for the bath lifetime. Furthermore, the lifetime increases as the concentration of ammonium citrate decreases. Films were electroplated from fresh solutions containing low ammonium citrate concentrations at different current densities and then at a fixed current density from aged solutions. The compositions of the deposited films were monitored using energy dispersive X-ray spectroscopy (EDS) within a scanning electron microscope (SEM).

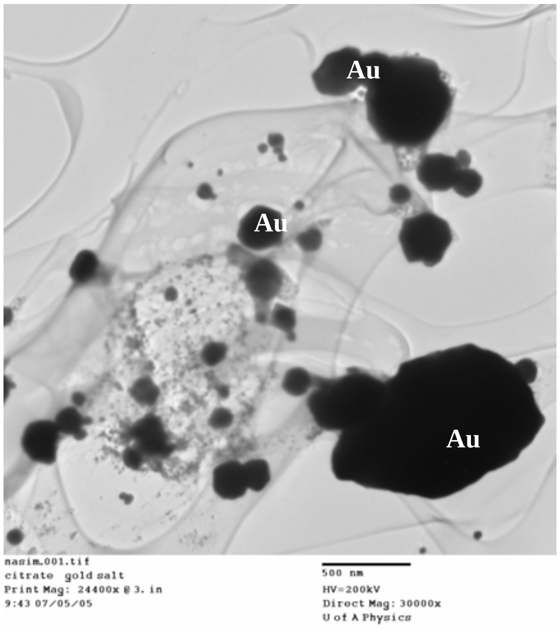


FIGURE II: TEM IMAGE SHOWING GOLD PRECIPITATES

Further experiments revealed that the plating rate was increased (by up to a factor of 3) as the concentration of gold and tin salts in the solution was increased (by up to a factor of 4). Plating rates were determined by measuring the thickness of the deposited films. Deposit thicknesses were measured in the SEM using cleaved cross-sections or through profilometry.

Although changes in the concentration of all bath constituents affect the process, only the most vital ones were chosen as key factors for these experiments due to time constraints.

BLACK BOX MODEL

To be able to model the Au-Sn electroplating process the system responses need to be identified. The two main categories of responses include stability and plating rate. The stability of each solution is monitored through turbidity tests. Turbidity measures the clarity of the solutions through light scattering. In other words, the turbidity value is related to amount of precipitates in the solution. A higher turbidity indicates reduced clarity. The time corresponding to the peak of the turbidity versus time curve is chosen as the shelf life.

The total plating rate of the multilayer film can be improved if the plating rate of each phase (AuSn and Au_5Sn) is improved. To be able to monitor the changes in the plating rate of each phase, the composition of each film should be taken into account. The plating rate for each run is measured through thickness measurements of the deposited films at three chosen current densities using profilometry. In addition, the compositions of the deposited films are monitored using EDS in an SEM.

The final Au-Sn 'black box' process model is shown in Figure III.

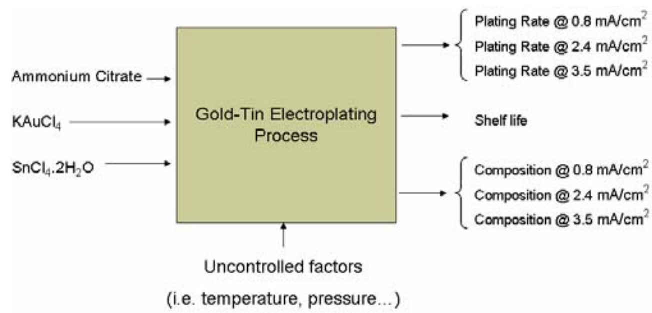


FIGURE III: BLACK-BOX MODEL OF THE GOLD TIN ELECTROPLATING PROCESS

DESIGN SELECTION

The experimental design can be chosen by considering the design objectives and the number of control factors. As mentioned previously, the objective of these experiments is to find improved and optimal process settings. Therefore, the experiment should be designed to allow for estimation of interaction and quadratic effects, while presenting an idea of the (local) shape of the response surface being investigated. These types of experiments are called response surface method (RSM) designs. Further, from screening tests three control factors are chosen. Using the design selection guideline table (TABLE II), either of the central composite or the Box-Behnken designs can be used [3].

TABLE II
DESIGN SELECTION GUIDELINES [3]

Number of Factors	Comparative Objective	Screening Objective	Response Surface Objective
1	1-factor completely randomized design	-	-
2 - 4	Randomized block design	Full or fractional factorial	Central composite or **Box-Behnken**
5 or more	Randomized block design	Fractional factorial or Plackett-Burman	Screen first to reduce number of factors

The Box-Behnken design was chosen, since it requires fewer runs compared with a central composite design for the case of three factors.

BOX-BEHNKEN DESIGN

The Box-Behnken design is an independent quadratic design. In this design, three levels of each factor are chosen. Experimental runs are conducted at the midpoints of edges of the cubic process space and at the center. Figure IV illustrates a Box-Behnken design for three factors [3].

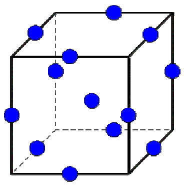


FIGURE IV: BOX-BEHNKEN DESIGN FOR 3 FACTORS [3]

TABLE III shows the experimental runs required for the Box-Behnken design of the Au-Sn plating process. The center point (sequence number 8) is repeated to provide a measure of process stability, inherent variability and to check for curvature. This repeated run is called sequence 16.

TABLE III
AU-SN BOX-BEHNKEN DESIGN

Sequence Number	Ammonium Citrate	$KAuCl_4$	$SnCl_2.2H_2O$
1	Low	High	Mid
2	Mid	High	Low
3	Mid	High	High
4	High	High	Mid
5	Low	Mid	Low
6	Low	Mid	High
7	Low	Mid	Mid
8	Mid	Mid	Mid
9	Mid	Mid	Low
10	High	Mid	High
11	High	Mid	Low
12	Low	Low	Mid
13	Mid	Low	Low
14	Mid	Low	High
15	High	Low	Mid

EXPERIMENTAL PROCEDURE

Solutions were prepared for each run of the Box-Behnken design. To obtain the responses for each run, films were electroplated at the three chosen current densities from a fresh solution, and the plating rates and compositions of the deposited films were determined. In addition, turbidity curves were obtained to determine the shelf life of each solution.

RESULTS

The compositions of the deposited films obtained using EDS are summarized in TABLE IV. The compositions between 10 and 20 at% tin are considered to be the Au_5Sn phase and are highlighted in blue (italic). The compositions between 45 and 55 at% tin are considered to be the AuSn phase and the values appear in red (bold). Any compositions between 20 and 45 at% are considered to be a mixture of the two phases and the values are in black. The plating rates measured through thickness measurements are also summarized in TABLE IV. However, these plating rate values are normalized with respect to the highest plating rate and have no units.

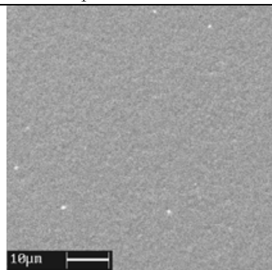
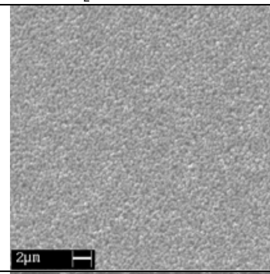
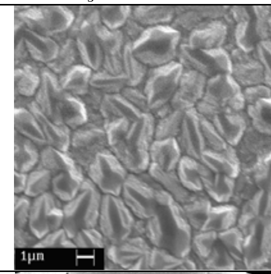
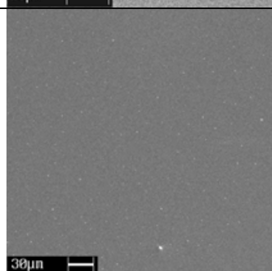
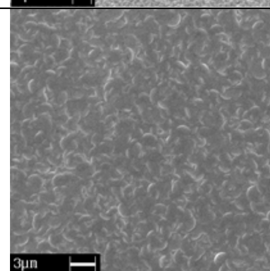
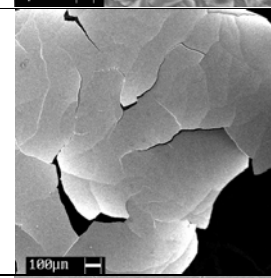
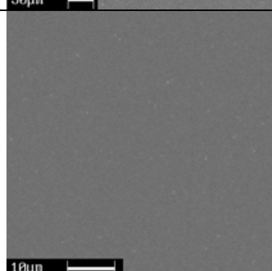
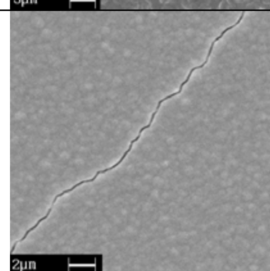
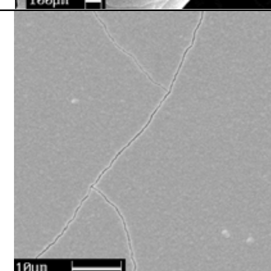
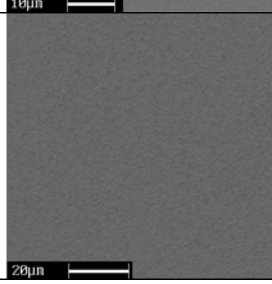
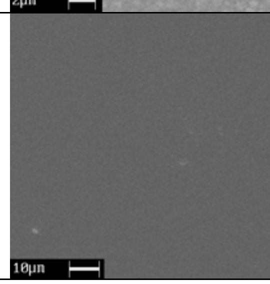
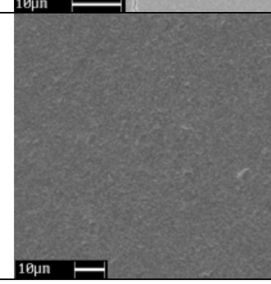
TABLE IV
COMPOSITION AND NORMALIZED PLATING RATES

Run	J_1= 0.8 mA/cm^2		J_2= 2.4 mA/cm^2		J_3= 3.5 mA/cm^2	
#	Sn at%	Rate	Sn at%	Rate	Sn at%	Rate
1	*15.5*	0.12	**49.0**	0.46	**49.2**	0.70
2	*15.8*	0.14	40.1	0.46	30.7	0.74
3	*15.9*	0.12	44.9	0.65	**49.7**	Stressed
4	*12.0*	0.15	39.5	0.60	43.3	0.95
5	34.9	0.20	**45.3**	0.60	39.3	0.71
6	35.0	0.11	34.8	0.44	39.3	0.60
7	*14.1*	0.07	34.3	0.54	38.0	0.92
8	*14.8*	0.09	42.5	0.45	**47.0**	1.00
9	*16.4*	0.14	44.9	0.51	37.0	0.80
10	*15.9*	0.10	**45.6**	0.49	**45.8**	0.59
11	*14.9*	0.15	41.5	0.67	33.3	0.71
12	**47.0**	0.10	**52.4**	0.49	**54.0**	0.75
13	43.8	0.19	40.4	0.30	**48.2**	0.53
14	42.0	0.17	**53.4**	0.44	**47.7**	0.56
15	40.3	0.17	**51.0**	0.42	43.2	0.64
16	*12.2*	0.07	38.6	0.54	**51.0**	0.93

Selected secondary electron SEM images of the deposited films are shown in TABLE V. The roughness of the deposited films increases as the current density increases (e.g., Run2). Also, in some runs an increase in the current density causes stress in the deposited films. Run 3 and 7 show examples of stressed films at high current densities. However, in some runs the increase in current density does not change the morphology of the deposits substantially (Run 9).

The shelf life data obtained from the turbidity curves are still being accumulated and will be ready for presentation at the conference. Furthermore, these results will be analyzed to obtain an optimized combination of the factors and this analysis will also be presented at the conference.

TABLE V
SECONDARY ELECTRON SEM IMAGES OF THE DEPOSITED FILMS

Run #	J_1= 0.8 mA/cm^2	J_2= 2.4 mA/cm^2	J_3= 3.5 mA/cm^2
2			
3			
7			
9			

CONCLUSIONS

The most effective factors influencing the lifetime and the plating rate of the Au-Sn plating process were determined, and a Box-Behnken design was used to optimize these factors. Multiple response optimizations will be performed using commercial software to analyze the data and to determine the optimal combination of solution components to both improve the stability and the plating rate.

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ACRONYMS

DOE: Statistical Design of Experiment
RSM: Response Surface Method
SEM: Scanning Electron Microscope(y)
TEM: Transmission Electron Microscope(y)