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# Redistribution of Pb-rich phase during electromigration in eutectic SnPb solder stripes

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The microstructural evolution occurring within the eutectic SnPb solder during electromigration is investigated utilizing Blech specimens. Solder stripes of about  $3\ \mu\text{m}$  in thickness were fabricated on Cu/Ti metallization. It was found that the Pb-rich phase ripened and aligned along the direction of the electron flow following the current stressing of  $9.7 \times 10^3\ \text{A}/\text{cm}^2$  at  $80\ ^\circ\text{C}$  for 24 h. As the stressing time or current density increased, the redistribution of the Pb-rich phase became more significant. Three-dimensional simulation was performed to examine the change in resistance and current-density distribution during electromigration. It was found that when the Pb-rich phase aligned along the direction of the electron flow, the total resistance of the solder stripe decreased. This reduction in total resistance may provide the driving force for the redistribution of the Pb-rich phase during electromigration. In addition, current crowding occurred in the vicinity of the interface of the Pb-rich and Sn-rich phases, creating a gradient of current density. This gradient might trigger the resistive Pb atoms to align along the direction of the electron flow. © 2006 American Institute of Physics. [DOI: 10.1063/1.2178392]

## I. INTRODUCTION

Flip-chip technology has become the most important packaging technique for high performance devices. One of its advantages is that a large number of tiny solder bumps can be fabricated into an area array on a chip as input/output (I/O) interconnections. However, to meet increasing performance requirements, the I/O density continues to increase. Thus, the size of the bumps progressively shrinks, causing rapid increases in the current density passing through each bump. The size of these solder bumps is currently  $100\ \mu\text{m}$  in diameter, and the design rule for packaging requires that each bump carries 0.2–0.4 A. The current density may reach  $(5\text{--}10) \times 10^3\ \text{A}/\text{cm}^2$  in the near future. Therefore, electromigration (EM) has become an important reliability issue for flip-chip joints.<sup>1,2</sup>

Eutectic SnPb solder has been implemented in flip-chip technology for decades due to its low melting point and excellent mechanical properties.<sup>3–5</sup> Therefore, the use of SnPb solder has been approved by the Committee on Waste from Electrical and Electronic Equipment (WEEE) in European countries and will continue until the year 2010. Since the SnPb solder is a binary alloy, including Pb-rich and Sn-rich phases, the diffusion behavior during electromigration is more complicated than that in Al or Cu.<sup>1</sup> Several studies have investigated the electromigration behavior in the SnPb alloy.<sup>6–10</sup> Liu *et al.* found that the dominant diffusion species was Sn atoms in a thin SnPb stripe when stressed at room temperature.<sup>7</sup> Huynh *et al.* conducted another electromigration study at  $150\ ^\circ\text{C}$  using V-groove samples and found that Pb atoms were the dominant diffusion species.<sup>8</sup> For flip-chip solder bumps, the Pb-rich phase migrates to the anode and

accumulates at this point.<sup>6,11</sup> This is because Pb atoms have higher diffusivity than Sn atoms at temperatures above  $151\ ^\circ\text{C}$ .<sup>12</sup>

However, the diffusion behavior near the device operation temperature of  $100\ ^\circ\text{C}$  is unclear. Moreover, the redistribution of Pb-rich phase at various temperatures in a Sn-rich matrix has not yet been studied. In this study, we use the edge displacement method to evaluate the electromigration behavior occurring within the SnPb solder film.<sup>13</sup> The redistribution of Pb-rich phase was investigated at the temperature range of  $80\text{--}100\ ^\circ\text{C}$ . Thus, this study provides a more fundamental understanding of the microstructure evolution occurring within eutectic SnPb alloy during electromigration.

## II. EXPERIMENT

Eutectic SnPb solder stripes of about  $1\text{--}2\ \mu\text{m}$  in thickness were fabricated in Si trenches according to the fabrication procedure described in our previous publication.<sup>13</sup> An appropriate amount of solder paste was reflowed on a  $0.4\ \mu\text{m}$  Cu film in the trench at  $210\ ^\circ\text{C}$  for 4 s on a hot plate. Then, the excess solder was polished away. Since the Si surface outside the trenches served as a polish stop, nice solder films with a smooth surface can be obtained. Figure 1(a) shows the cross-sectional schematic for a SnPb solder stripe in the Si trench. The dimensions of the solder stripe were  $80\ \mu\text{m}$  in width,  $370\ \mu\text{m}$  in length, and  $3.1\ \mu\text{m}$  in thickness. An intermetallic compound (IMC) of  $\text{Cu}_6\text{Sn}_5$  was formed following the reflow. Solder stripes with a smooth surface can be fabricated by this technique. Figure 1(b) shows the plan-view scanning electron microscopy (SEM) image of a fabricated Blech specimen, and the middle solder stripe is of interest. A desired current was applied through the two pads on the two ends by two probes on a hot plate. The test structure is also known as the Blech specimen.<sup>14</sup>

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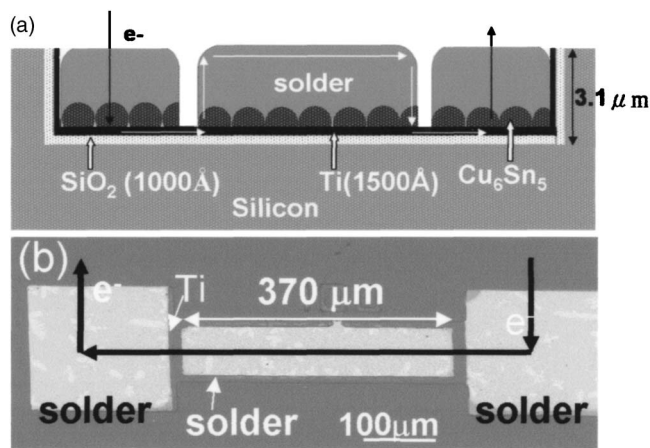


FIG. 1. (a) Cross-sectional schematic of solder Blech specimens fabricated inside a Si trench. (b) Plan-view SEM image of the fabricated solder stripe on the Cu/Ti metallization layer. The SnPb stripe was  $370 \mu\text{m}$  long,  $80 \mu\text{m}$  wide, and approximately  $3.1 \mu\text{m}$  thick.

The increase in temperature due to the Joule heating effect was monitored by a Quantum Focus Instruments (QFI) infrared microscope, which has a  $0.1 \text{ }^\circ\text{C}$  temperature resolution and a  $2 \mu\text{m}$  spatial resolution.<sup>15</sup> SEM and elemental dispersive spectrum (EDS) were used to examine the microstructure evolution and composition of the solder, respectively. The average thickness of the IMC layer was  $0.6 \mu\text{m}$ , with approximately 80% of the applied current drifting in the solder stripe, 19% in the IMC layer, and only 1% in the Ti layer. The current density mentioned in this paper refers to the value in the solder stripe. The temperature increase due to the Joule heating effect was only  $1.8 \text{ }^\circ\text{C}$  for the most severe stressing condition in this study. This may be due to the large area available for heat dissipation and the excellent heat conduction in the Si substrate. Therefore, the Joule heating effect was not serious in the solder Blech specimen.

To provide a better understanding of how a current could alter the microstructure of the eutectic SnPb alloy, a three-dimensional (3D) simulation on current-density distribution was performed. The simulation models used in this study are shown in Figs. 2(a)–2(c) schematically. The dimensions of the solder stripe were  $70 \mu\text{m}$  in length,  $35 \mu\text{m}$  in width, and  $10 \mu\text{m}$  in thickness. The first model shows the extreme case where all the Pb-rich phase aligned perpendicular to the direction of the electron flow, as depicted in Fig. 2(a). In the second model, all the Pb-rich phase lined up parallel to the direction of the electron flow, as shown in Fig. 2(b). In the third model, the Pb-rich grains were assumed to be rectangles and were evenly distributed in the Sn-rich matrix. In the three models, the volume of the Pb-rich phase was 29% based on the Sn–Pb binary phase diagram. In these simplified models, only the solder stripe was considered. A current was applied through the two ends of the solder stripe, and a constant current of 0.175 A was applied, which corresponds to a current density of  $5 \times 10^4 \text{ A/cm}^2$ . At  $100 \text{ }^\circ\text{C}$ , the resistivity of the Pb-rich and Sn-rich phases used in this simulation are 24.9 and 14.1, respectively. ANSYS software was used to perform the simulation in this study, and the model used was a SOLID5 eight-node hexahedral coupled field element. The dimension of the mesh was  $0.5 \mu\text{m}$ .

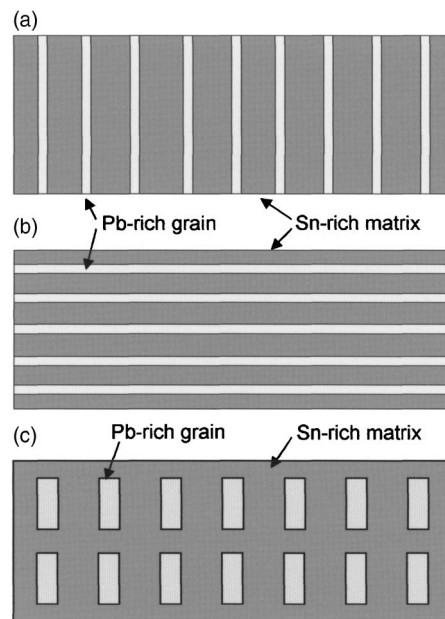


FIG. 2. Simulation models used in this study. (a) All the Pb-rich stripes aligned perpendicular to the direction of the electron flow. (b) All the Pb-rich stripes aligned parallel to the direction of the electron flow. (c) Regular arrays of rectangular Pb-rich grains in the continuous Sn-rich matrix.

### III. RESULTS

The microstructural evolution of the SnPb solder during electromigration is shown in Figs. 3(a)–3(d). The solder stripe was applied by  $9.7 \times 10^3 \text{ A/cm}^2$  at  $80 \text{ }^\circ\text{C}$ . Figure 3(a) illustrates the microstructure for the as-fabricated SnPb stripe. The white regions represent the Pb-rich grains. Since the sample was taken out of the hot plate after reflowing for 4 s, most of the Pb-rich phase is finely distributed in the Sn-rich matrix, although some of them aggregated as large clusters. Figures 3(b)–3(d) show the microstructure follow-

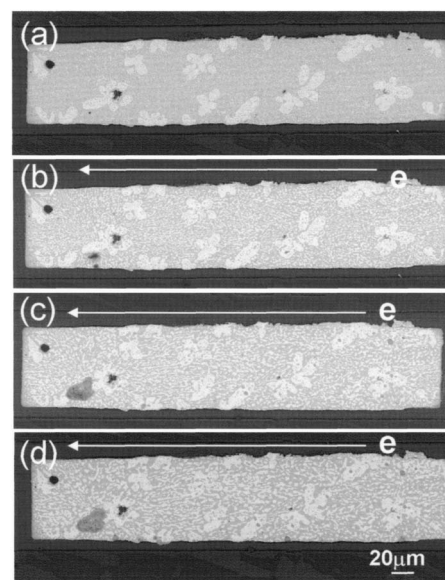


FIG. 3. Plan-view SEM images showing the microstructural evolution for a solder stripe stressed by  $9.7 \times 10^3 \text{ A/cm}^2$  at  $80 \text{ }^\circ\text{C}$  for (a) 0 h, (b) 24 h, (c) 72 h, and (d) 162 h. Pb-rich phase ripened and aligned in the direction of the electron flow after 24 h stressing, and it became more obvious as the stressing time increased.

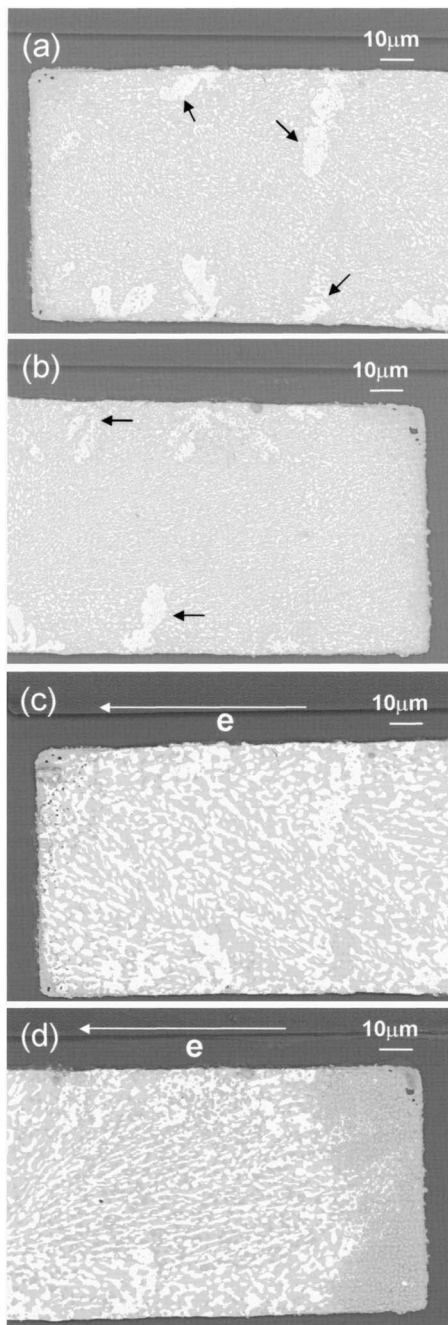


FIG. 4. SEM images for another solder stripe stressed by the current density of  $1.1 \times 10^5$  A/cm<sup>2</sup> at 100 °C. (a) Anode end prior to current stressing, (b) cathode end prior to current stressing, (c) anode end following 14.0 h, and (d) cathode end following 14.0 h. Significant redistribution of Pb-rich phase along the direction of the electron flow was observed.

ing stressing for 24, 72, and 162 h, respectively. As the stressing time increased, the finely dispersed Pb-rich phase ripened, and the large clusters were gradually dissolved. Moreover, the ripened Pb-rich grains aligned roughly in the long direction, i.e., the direction parallel to the electron flow.

This interesting phenomenon became more noticeable at a higher stressing temperature and current density. Figures 4(a) and 4(b) show the microstructure prior to current stressing, whereas Figs. 4(c) and 4(d) show the microstructure on the anode and the cathode ends, respectively, after the stressing by  $1.1 \times 10^5$  A/cm<sup>2</sup> at 100 °C for 14.0 h. It can be seen

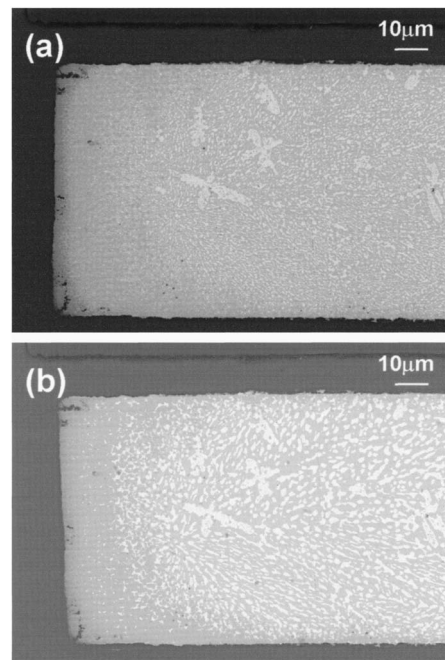


FIG. 5. A solder stripe that experienced thermal aging only. (a) Prior to the aging treatment. (b) Following the aging treatment at 100 °C for 14.0 h on a hot plate.

that more Pb-rich grains aligned parallel to the direction of the electron flow. Furthermore, some of the Pb-rich clusters, which initially aligned perpendicular to the electron flow, were destroyed and aligned parallel to the electron flow after current stressing. As indicated by the arrows in Figs. 4(a) and 4(b), the Pb-rich clusters were redistributed after the current stressing.

To separate the thermal aging effect on the Pb-rich distribution, another sample was aged at 100 °C for 14.0 h on a hot plate. Figures 5(a) and 5(b) show the microstructures before and after the aging treatment. The ripening effect also occurred for the Pb-rich phase, and it grew larger after the aging. Some of the Pb-rich grains seem to possess a texture after the aging, and they aligned approximately in a lengthways direction. However, the alignment of the Pb-rich grains is not significant compared with the results shown in Fig. 4. As a result, it can be concluded that the alignment of the Pb-rich grains along the electron flow is mainly a consequence of the current stressing.

To investigate the driving force for the Pb-rich grains aligning along the direction of the electron flow, 3D simplified modeling was performed to examine the resistance of the stripe and the current distribution in the two phases. First, two extreme cases were examined, as illustrated in Figs. 2(a) and 2(b), i.e., when all the Pb-rich grains were perpendicular or parallel to the direction of the electron flow. Figure 6(a) shows the current distribution in the first model with Pb-rich grains perpendicular to the direction of the electron flow and the current distributed uniformly throughout the solder stripe. However, current crowding occurs in the solder stripe when the all of the Pb-rich phase was parallel to the direction of electron flow, as shown in Fig. 6(b). Since the Pb atom is about twice as resistive as the Sn atoms, the current density in the Sn-rich phase was about twice that of the Pb-rich

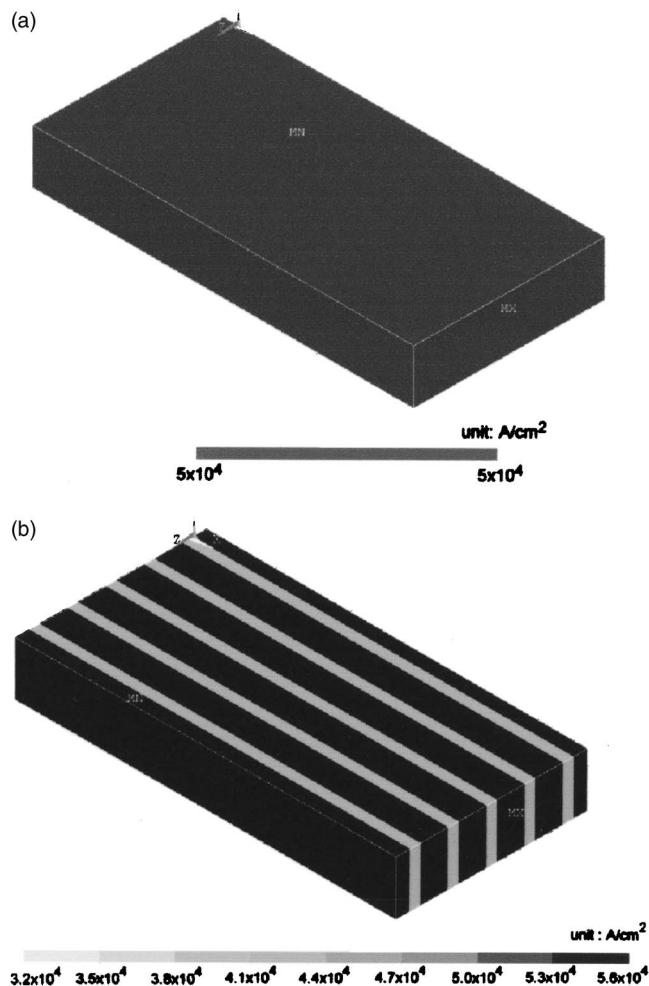


FIG. 6. Simulation results showing the current-density distribution (a) in the first model with all the Pb-rich phase perpendicular to the direction of the electron flow and (b) in the second model with all Pb-rich phase parallel to the direction of the electron flow.

phase. Moreover, the resistance for the second model was  $32.2 \text{ m}\Omega$ , which was lower than the figure of  $34.3 \text{ m}\Omega$  for the first model. This indicates that when the Pb-rich phase aligns parallel to the direction of the electron flow, the resistance of the solder stripe would be reduced. The difference in resistance for the two models was about 6.5%. As a result, the Joule heating effect will be lower when the Pb-rich grains line up along the direction of the electron flow. The reduction in resistance may provide the driving force for the Pb-rich phase to align along the direction of the electron flow.

Furthermore, the current-density distribution in the vicinity of the interface of the Pb-rich and Sn-rich phases was also investigated by simulation. Figure 7(a) shows the current-density distribution in regular arrays of rectangular Pb-rich grains in the Sn-rich matrix, as illustrated in Fig. 2(c). The positions of the Pb-rich grains were marked by the dotted lines. The resistance of the model is  $33.3 \text{ m}\Omega$ , which is between the values of the two extreme cases. As electrons encounter the Pb-rich grains, some of them may detour and crowd into the neighboring Sn-rich phase due to the higher resistivity of Pb atoms. The minimum current density occurred at the centers of the Pb-rich grains, whereas the maximum took place at the edges of the Pb-rich phase, as indi-

cated in Fig. 7(b). The ratio of maximum and minimum current density in the stripe was only 1.2. Although the crowding effect is not serious, there is a gradient of current density in the vicinity of the interface. Figure 7(c) shows the current density near a rectangular Pb-rich grain. The gradient of current density was estimated to be  $2.2 \times 10^7 \text{ A/cm}^3$  when applied by  $5 \times 10^4 \text{ A/cm}^2$ . Furthermore, the gradient increased linearly as the applied current increased. Figure 7(d) shows the gradient of current density as a function of applied current density. As the applied current density increased to  $1.0 \times 10^5 \text{ A/cm}^2$ , the gradient increased to  $4.4 \times 10^7 \text{ A/cm}^3$ .

#### IV. DISCUSSION

Similar phenomena can be found in flip-chip solder joints during electromigration. Nah *et al.* performed an electromigration test in high-Pb/eutectic SnPb composite bumps, and they found that the Sn atom in the eutectic SnPb solder diffused to high-Pb solder in the chip side.<sup>16</sup> In addition, the Sn-rich phase aligned along the direction of the electron flow in the high-Pb matrix as it approached the chip side. Although they did not discuss the issue, the phenomena can be clearly observed in their cross-sectional SEM images. In addition, it has been reported that the resistance of pure Sn stripes was reduced following current stressing,<sup>17,18</sup> and rotation of Sn grains as well as the grain growth of low-resistance grains were proposed for the resistance reduction in the pure Sn stripe.

In these simplified models, only the solder stripe was considered, and currents were applied through its two ends. We neglected the current crowding regions on the two ends of the stripe. Based on the simulation results performed by Yeh and Tu,<sup>19</sup> the current crowding effect occurred at the two ends of the Blech specimen, but only within a few micrometers from the edge of the stripe. Therefore, in the solder Blech stripe that is  $370 \mu\text{m}$  long, the current is expected to be uniform inside the solder stripe except at the two ends.

Under a higher stressing current, the Pb-rich phase redistributed faster for the following two reasons. Firstly, the difference in Joule heating becomes larger at a higher stressing current. The driving force for the redistribution may be proportional to  $I^2(\Delta R)$ , where the  $\Delta R$  is the reduction in resistance due to the redistribution of Pb-rich phase. Secondly, the gradient force increases as the applied current increases. As shown in Fig. 7(d), the gradient increased 100 times when the current density increased from  $10^3$  to  $10^5 \text{ A/cm}^2$ . In addition, at a higher stressing temperature, the diffusivity of the Pb and Sn atoms become higher. Therefore, the Pb-rich grains noticeably redistributed themselves after the stressing by  $1.1 \times 10^5 \text{ A/cm}^2$  at  $100 \text{ }^\circ\text{C}$  for 14.0 h, as shown in Figs. 4(c) and 4(d). It is noteworthy that the redistribution may be a metastable state. As the stressing time increases, either the Pb or Sn atoms may accumulate on the anode side, depending on the stressing temperature. For example, when the solder is stressed at  $150 \text{ }^\circ\text{C}$ , Pb atoms are the dominant diffusion species. Therefore, Pb atoms will accumulate on the anode side after stressing for a long time.<sup>8,20</sup> On the other hand, Sn atoms will accumulate on the anode side if the solder is stressed at room temperature.<sup>7</sup>

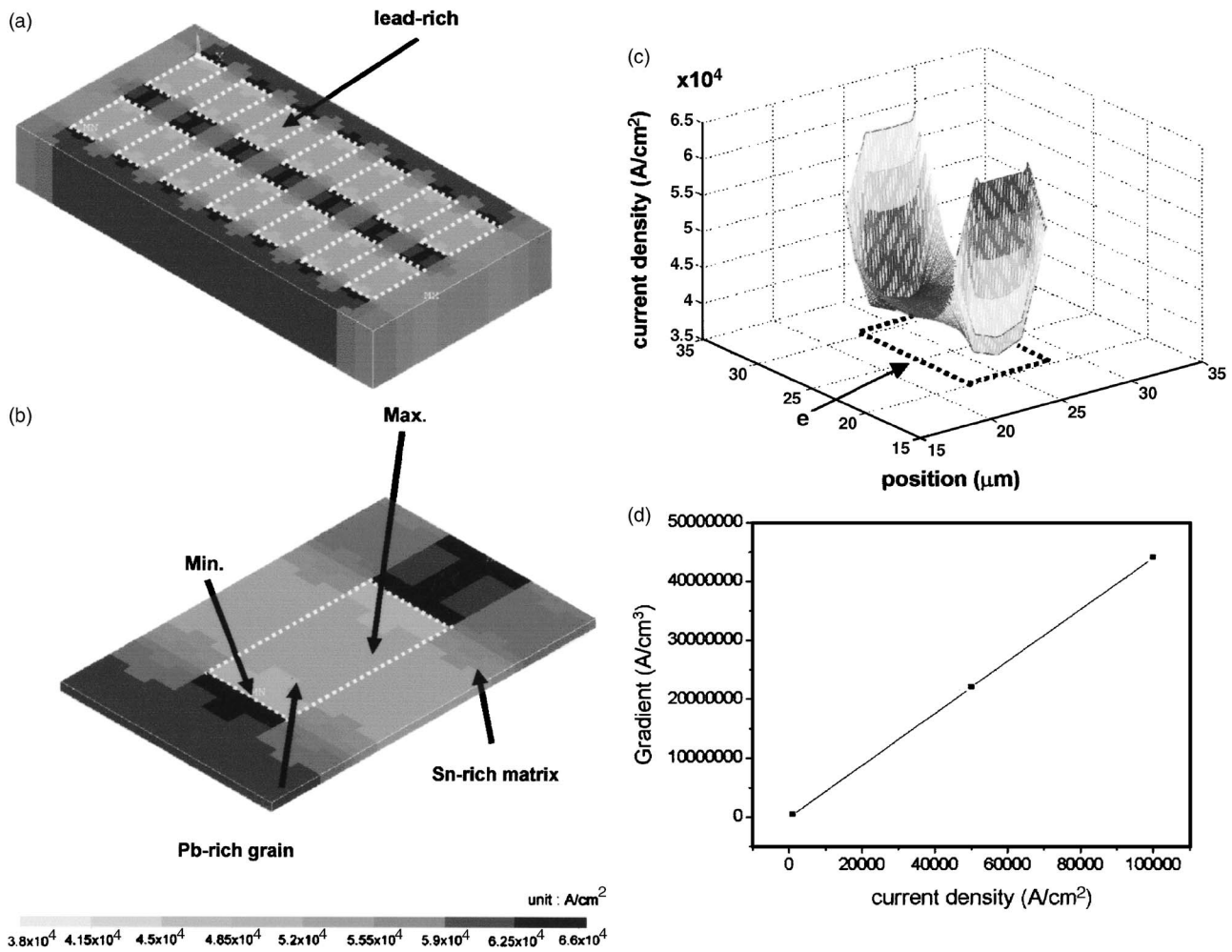


FIG. 7. (a) Current-density distribution in regular arrays of rectangle Pb-rich grains in the Sn-rich matrix. (b) Enlarged image for the results in (a), showing current-density distribution around a Pb-rich grain. (c) Corresponding current-density profile in (b). (d) Gradient of current density as a function of applied current density.

Tu *et al.* proposed that resistive atoms or vacancies would move to low current-density regions during current stressing.<sup>21</sup> In electromigration for Al and Cu interconnections, voids may form in the low current-density region.<sup>22,23</sup> In the binary system studied here, Pb was the resistive atom, and it might move to the low current-density region during current stressing, resulting in the Pb-rich phase aligned along the direction of the electron flow. As shown in Fig. 7(d), the gradient may be larger than  $10^7$  A/cm<sup>3</sup> when the applied current density was larger than  $10^5$  A/cm<sup>2</sup>. To examine whether the gradient force is large enough to cause the Pb atoms to move to the low current-density region, both the electromigration and the gradient forces were estimated. The electromigration force is

$$F_{EM} = Z^* e E, \quad (1)$$

where  $Z^*$  is the effective charge number,  $E$  is the electrical field, and  $e$  is the charge for an electron. For the sample in Fig. 4, the electromigration force was estimated to be 7 eV/cm when the stripe was stressed at 0.096 A and the effective charge number of the Pb atom is assumed to be 47. On the other hand, the driving force due to the gradient of current density can be expressed as<sup>21</sup>

$$F_{\text{gradient}} = \frac{dP}{dr} = \frac{d(qjAR)}{dr}, \quad (2)$$

where  $P$  is potential,  $r$  is distance,  $q$  is the charge number of Pb atoms,  $j$  is current density,  $A$  is the scattering cross section of the Pb atoms, and  $R$  is the resistance. Since we are considering migrating Pb atoms, we may take  $q$  to be the same as their effective charge number. The current density was taken as the average current density in the solder stripe in Fig. 4, which was  $1.1 \times 10^5$  A/cm<sup>2</sup>. The typical scattering cross section for Pb atoms was  $5 \times 10^{-14}$  cm<sup>2</sup>.<sup>24</sup> The resistance of a Pb atom is assumed to be  $10^3 \Omega$ .<sup>21</sup> The distance was taken as  $0.5 \mu\text{m}$ . Thus, the gradient force is estimated to be 0.5 eV/cm. The gradient force is approximately one order smaller in magnitude than the electromigration force. Therefore, the gradient force may cause the Pb atoms to move to the region of low current density. During electromigration, when the Pb atoms move to the low current-density region, the Pb-rich grains might grow along the direction of the electron flow. Therefore, the gradient force might trigger the redistribution of the Pb-rich phase during electromigration in solder.

## V. CONCLUSIONS

The microstructural evolution in the SnPb solder during electromigration has been studied using thin solder stripes. Pb-rich phase redistribution was found to run along the direction of the electron flow after high current-density stressing at 80 and at 100 °C. Simulation results indicated that the redistribution of the Pb-rich phase would lower the total resistance of the solder stripe and thus would reduce the Joule heating effect during current stressing. This reduction in the resistance may provide the driving force for the redistribution of Pb-rich phase in the Sn-rich matrix.

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<sup>1</sup>K. N. Tu, J. Appl. Phys. **94**, 5451 (2003).

<sup>2</sup>*The International Technology Roadmap for Semiconductor 2003* (Semiconductor Industry Association, San Jose, CA, 2003).

<sup>3</sup>K. N. Tu and K. Zeng, Mater. Sci. Eng., R. **R34**, 1 (2001).

<sup>4</sup>L. F. Miller, IBM J. Res. Dev. **13**, 239 (1969).

<sup>5</sup>P. A. Totta and R. P. Sopher, IBM J. Res. Dev. **13**, 226 (1969).

<sup>6</sup>S. Brandenburg and S. Yeh, *Proceedings of the Surface Mount International Conference and Exhibition, SM198, San Jose, CA, 23–27 August 1998* (SMTA, Edina, MN, 1998), p. 337.

<sup>7</sup>C. Y. Liu, Chih Chen, and K. N. Tu, J. Appl. Phys. **88**, 5703 (2000).

<sup>8</sup>Q. T. Huynh, C. Y. Liu, Chih Chen, and K. N. Tu, J. Appl. Phys. **89**, 4332 (2001).

<sup>9</sup>T. Y. Lee, K. N. Tu, S. M. Kuo, and D. R. Frear, J. Appl. Phys. **89**, 3189 (2001).

<sup>10</sup>H. Ye, C. Basaran, and D. Hopkins, Appl. Phys. Lett. **82**, 7 (2003).

<sup>11</sup>G. A. Rinne, Microelectron. Reliab. **43**, 1975 (2003).

<sup>12</sup>D. Gupta, K. Vieregge, and W. Gust, Acta Mater. **47**, 5 (1999).

<sup>13</sup>Y. T. Yeh, C. K. Chou, Y. C. Hsu, C. Chen, and K. N. Tu, Appl. Phys. Lett. **86**, 203504 (2005).

<sup>14</sup>I. A. Blech, J. Appl. Phys. **47**, 1203 (1976).

<sup>15</sup>T. L. Shao, S. H. Chiu, Chih Chen, D. J. Yao, and C. Y. Hsu, J. Electron. Mater. **33**, 1350 (2004).

<sup>16</sup>J. W. Nah, K. W. Paik, J. O. Suh, and K. N. Tu, J. Appl. Phys. **94**, 7560 (2003).

<sup>17</sup>A. T. Wu, K. N. Tu, J. R. Lloyd, N. Tamura, B. C. Valek, and C. R. Kao, Appl. Phys. Lett. **85**, 2490 (2004).

<sup>18</sup>J. R. Lloyd, Appl. Phys. Lett. **94**, 6483 (2003).

<sup>19</sup>E. C. C. Yeh, and K. N. Tu, J. Appl. Phys. **89**, 3203 (2001).

<sup>20</sup>G. A. Rinne, Microelectron. Reliab. **43**, 1975 (2003).

<sup>21</sup>K. N. Tu, C. C. Yeh, C. Y. Liu, and Chih Chen, Appl. Phys. Lett. **76**, 988 (2000).

<sup>22</sup>C. K. Hu, L. Gignac, S. G. Malhotra, R. Rosenberg, and S. Boettcher, Appl. Phys. Lett. **78**, 904 (2005).

<sup>23</sup>S. Shingubara, T. Osaka, S. Abdeslam, H. Sakaue, and T. Takahagi, AIP Conf. Proc. **491**, 138 (1999).

<sup>24</sup>M. C. Gutzwiller, in *Atomic and Electronic Structure of Metals*, edited by J. J. Gilman and W. A. Tiller (American Society for Metals, Metals Park, OH, 1966), Chap. 12.