

Microstructural aspects and mechanism of the C49-to-C54 polymorphic transformation in titanium disilicide

Z. Ma^{a)} and L. H. Allen

Department of Materials Science and Engineering and Coordinated Science Laboratory,
University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

D. D. J. Allman

Microelectronic Products Division, AT&T Global Information Solutions, Colorado Springs, Colorado 80916

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Microstructural study of the C49-TiSi₂ to C54-TiSi₂ polymorphic transformation has been performed to elucidate microstructural evolution and possible mechanism of the phase transformation. It has been shown that the nucleation of the C54-TiSi₂ is heterogeneous, and preferentially takes place at triple grain junctions or grain boundaries. The interphase interfaces between C49 and C54 disilicides are often ragged with incoherent characteristics. The growth of the C54 phase is found to proceed by advancing the highly mobile incoherent interfaces in all directions toward the heavily faulted C49 phase. No rigorous orientation relationships are found between the two phases. The microstructural features of the transformation bear some massive characteristics. © 1995 American Institute of Physics.

I. INTRODUCTION

Polymorphism is recognized as the ability of the same chemical compound to exist in more than one crystalline structure and is very common phenomenon found in nature. Many transition metal silicides (such as FeSi₂ and Co₂Si) and refractory metal silicides (such as TiSi₂ and MoSi₂) possess more than one crystalline structure. The technologically important titanium disilicide was discovered to have two crystalline forms: one with a base-centered-orthorhombic structure (C49-TiSi₂: $a=0.362$ nm, $b=1.376$ nm, $c=0.360$ nm) and the other with a face-centered-orthorhombic structure (C54-TiSi₂: $a=0.825$ nm, $b=0.478$ nm, $c=0.854$ nm).¹ The C49 phase does not appear in the Ti-Si bulk equilibrium phase diagram² and forms during low-temperature annealing of a Ti/Si thin-film couple (500–600 °C)^{3,4} or crystallization of a codeposited, stoichiometric amorphous Ti_{0.33}Si_{0.67} alloy (about 390 °C).⁵ It is often highly resistive (about 60–100 μΩ cm) as compared with the equilibrium C54 phase, which has an electrical resistivity of about 15 μΩ cm and is currently being used as interconnects and contacts in Si-based metal-oxide-semiconductor field-effect transistors. It has been shown that the C49 phase is inevitable during microelectronic processing and the desired low resistivity C54 disilicide can only be obtained by thermally transforming the metastable C49 polymorph at elevated temperatures (≥650 °C).^{6–8}

Since the C49-to-C54 phase transformation is of particular technological interest, there have been considerable studies on this structural transition. Most of them were focused on the effect of processing conditions such as dopants^{7,9} and linewidth¹⁰ on the transformation. Antimony is found to enhance the structural conversion, while arsenic¹¹ retards it. Lasky *et al.*¹⁰ reported that the effect of linewidth on the C49-to-C54 transformation in patterned C49-TiSi₂

fine lines. They found that the transformation is significantly difficult on the submicrometer lines. It has been suggested that more nucleation events for the C54 phase be required to completely transform narrow lines of C49 phase into C54 phase lines. However, very little is known about the microstructural details of this structural transformation and its possibly associated mechanism. In order to provide a fundamental basis for explaining various interesting experimental results and to effectively control the microstructure during processing, a study of the microstructural aspects of the transformation appears very useful.

In this paper, we present a microstructural study of various stages of the C49-to-C54 phase transformation in titanium disilicide using transmission electron microscopy (TEM) and selected area electron diffraction. Both nucleation and growth of the C54-TiSi₂ within polycrystalline C49-TiSi₂ have been described in detail. A possible mechanism of the transformation will be suggested in the light of the main microstructural characteristics observed.

II. EXPERIMENTAL PROCEDURE

The samples used in this work were prepared using *p*-type Si (100) substrates with a 750-nm-thick thermal oxide. After chemical cleaning, about 350 nm of phosphorus doped polycrystalline Si (poly-Si) film was first grown onto the oxidized Si wafers using low-pressure chemical-vapor deposition. The samples were then dipped in a dilute HF solution just prior to loading into a sputter-deposition system with a base pressure of 2×10^{-8} Torr. 55–65 nm Ti film was deposited over the poly-Si. The samples were so constructed to meet the needs for *in situ* sheet resistance measurement.¹² The thermal oxide serves as electrical isolation between the deposited Ti/Si bilayer and the Si substrate. The advantage of the *in situ* resistance measurement is that it gives a real-time track of thin-film reaction by monitoring the change of tem-

^{a)}Present address: Digital Equipment Corporation, Advanced Semiconductor Development, HLO2-3/N08, 77 Reed Road, Hudson, MA 01749.

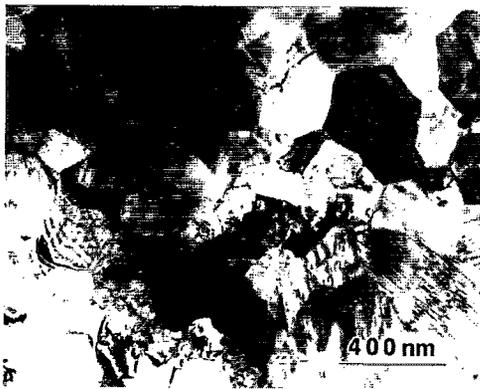


FIG. 1. A plan-view TEM micrograph of the $C49\text{-TiSi}_2$, showing heavily faulted, polycrystalline $C49$ grains, taken from samples after anneal at 600°C for 1 h.

perature coefficient of resistance during annealing, and also aids in obtaining critical samples at various stages of the transformation.

The samples were first annealed in high vacuum (5×10^{-8} Torr) at 600°C for 1 h to obtain a fully reacted $C49\text{-TiSi}_2$ film. During annealing, sheet resistance of the bilayer was used to monitor the progress of the silicide formation. The annealed samples were also examined using x-ray diffraction and TEM for the starting microstructure of the $C49$ phase. For transformation study, annealing was carried out isothermally over a temperature range of $650\text{--}750^\circ\text{C}$ for various times. Microstructure and morphology were characterized in a Philips CM-12 transmission electron microscope operated at 120 kV, with an emphasis on the nucleation and growth of the $C54\text{-TiSi}_2$. Plan-view TEM specimens were prepared using backside polishing down to $\sim 30\ \mu\text{m}$, followed by a cold-trap ion milling to electron transparency. Some samples were also studied using a Hitachi H-9000 transmission electron microscope operated at 300 kV.

III. RESULTS AND DISCUSSION

Figure 1 shows a bright-field image of the plan-view samples after the first annealing step. The electron-diffraction analysis indicates that all the Ti film reacted with the poly-Si to form a polycrystalline $C49\text{-TiSi}_2$, which is approximately equiaxed with an average grain size of 300 nm. As seen in the picture, the $C49\text{-TiSi}_2$ phase is heavily faulted. A chemical analysis was also done on the samples using Auger electron spectroscopy. It is found that the composition of $C49\text{-TiSi}_2$ film is fairly uniform through the entire layer and is nearly stoichiometric (i.e., $\text{Ti}_{0.33}\text{Si}_{0.67}$). High-resolution imaging was also used to examine its defective nature. Figure 2(a) and 2(b) show a high-resolution image of the $C49\text{-TiSi}_2$ structure projected along the $[100]$ zone axis and the corresponding selected area diffraction pattern, respectively. The faults are visible when viewed in either the $[100]$ or $[001]$ zone axis and disappear in the $[101]$ projection. These planar defects cause streaking (rel-rods) in reciprocal space. Diffraction analyses reveal that most of the stacking fault is a 90° -rotation twin which changes the a axis

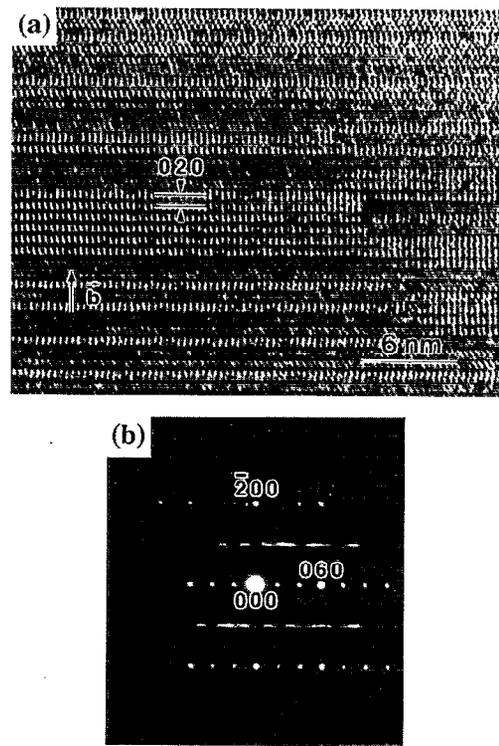


FIG. 2. (a) High-resolution TEM image of the $C49\text{-TiSi}_2$ structure viewed along $[100]$ zone axis. The stacking faults are revealed in the b direction with a displacement vector $(a+c)/2$. (b) The corresponding $[100]$ zone axis electron-diffraction pattern. Note that there is 90° rotation between two photos.

into the c axis. The twin habit plane is (010) . Similar results have recently been reported by Bourret *et al.*¹³ and Jia *et al.*¹⁴

Nucleation and growth of the $C54\text{-TiSi}_2$ were studied during the second annealing step. Figure 3(a) is a planar view TEM image of a sample annealed at 680°C for 30 min, showing the early stage of the transformation. A $C54\text{-TiSi}_2$ nucleus is observed to form at grain boundaries of the $C49\text{-TiSi}_2$. Figure 3(b) gives a magnified picture of the $C54$ nucleus with its microdiffraction pattern shown as an inset. The interface between the $C54$ nucleus and the lower $C49$ grain is mostly smoothly curved, indicating its incoherent characteristics. But its upper interphase boundary exhibits some coherency, as demonstrated by the faceted interface.¹⁵ Like all other solid-state transformations, the occurrence of local coherency would lower interphase boundary energy, thereby reducing the energy barrier for critical nucleus formation. In addition to grain-boundary nucleation, the $C54\text{-TiSi}_2$ was also found to nucleate at triple grain junctions of the $C49$ phase, as is shown in Fig. 4(a) and 4(b) taken from samples annealed at 700°C for 15 min. Statistical examinations reveal that nucleation at triple grain junctions is more prevalent. It has also been noticed that among the available heterogeneous sites (including grain boundaries and triple grain junctions), only about 15% of grain boundaries and triple grain boundaries were taken. This may be indicative of the difficulty of nucleating the $C54$ silicide.

In most cases, polymorphic transformation in intermetallic compounds is accompanied by a very small heat effect,

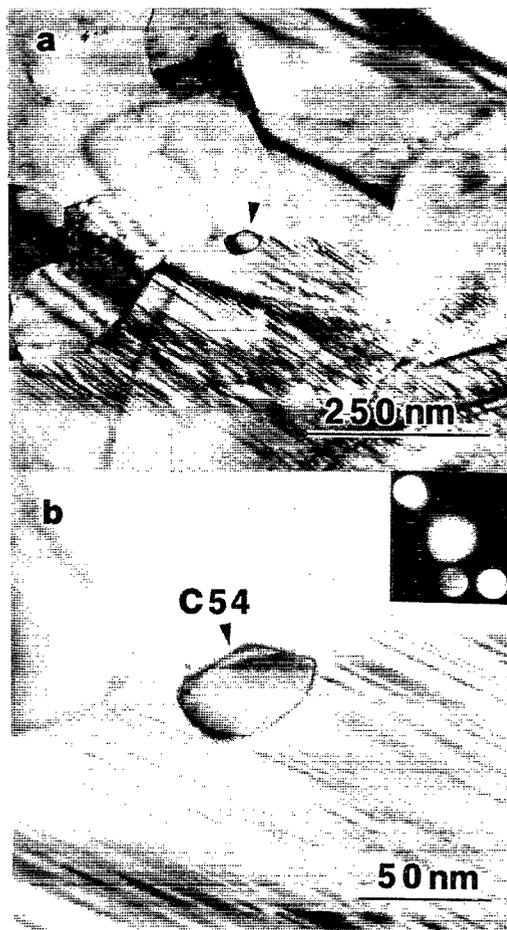


FIG. 3. (a) A plan-view TEM micrograph taken from a sample annealed at 680 °C for 30 min, showing the nucleation of $C54\text{-TiSi}_2$ at grain boundaries of $C49\text{-TiSi}_2$ (indicated by arrows), and (b) a magnified view of the $C54$ nucleus and its microdiffraction pattern shown as an inset. Note that the interface between the $C54$ nucleus and the lower $C49$ grain is smoothly curved, indicating its incoherent characteristics.

typically ranging from 0.01 to 0.03 eV/atom.¹⁶ Although there is no data available on the $C49\text{-to-}C54$ transformation, the bulk free-energy difference ΔG_p between $C49\text{-TiSi}_2$ and $C54\text{-TiSi}_2$ is expected to be very small. Since the nucleation energy barrier is inversely proportional to ΔG_p , and therefore would be very large for the $C54$ phase, the nucleation of the $C54$ disilicide is very difficult and often occurs heterogeneously, as was observed in our samples. The adoption of triple grain junctions for nucleation would further reduce this energy barrier based upon an analysis made by Clemm and Fisher.¹⁷

The morphological development and crystallographic information between the $C49$ and $C54$ disilicides were also examined. Our preliminary results do not show any rigorous orientation relationships between the two phases. This can also be expected from the largely incoherent nature of the interphase boundaries. Figures 5(a) and 6(a) show bright-field images of the typical interface morphology of the coexisting $C49$ and $C54$ phases. These were taken from samples after annealing at 700 °C for 75 min. As seen in these micrographs, the $C54$ phase grows by consuming the heavily

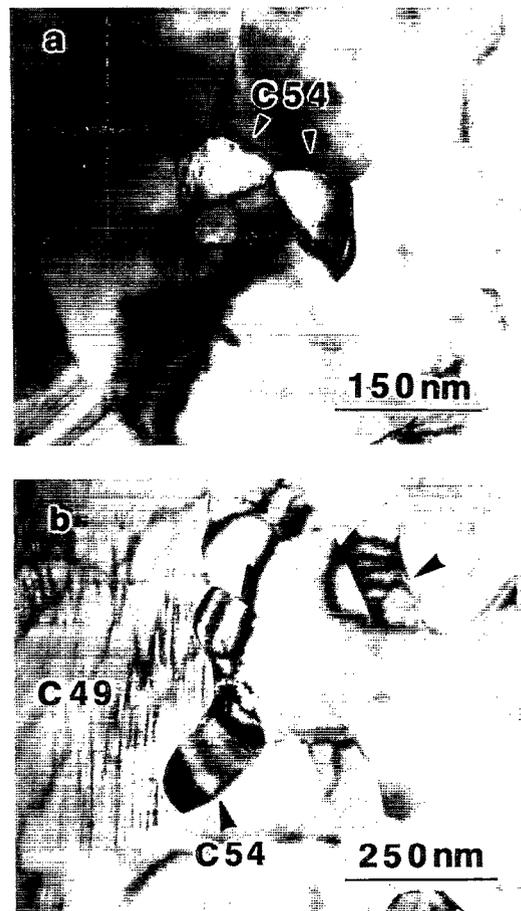


FIG. 4. TEM micrographs taken from samples annealed at 700 °C for 10 min (a) showing preferred nucleation of the $C54\text{-TiSi}_2$ at triple grain junctions of the $C49\text{-TiSi}_2$ and (b) incoherent interphase interfaces between the coexisting $C49$ and $C54$ phases.

faulted $C49$ phase. The growth front is very ragged, implying incoherent characteristics of the growth front. This is also confirmed by several zone axis diffraction analyses, for example, as shown in Figs. 5(b) and 6(b), where the $C54$ phase was aligned with a particular zone axis while the $C49$ phase is away from zone axis (the streaks due to the $C49$ phase are indicated by arrows).

Another salient morphological feature, which is often observed in our samples, is that certain $C54$ grains were able to grow across many small $C49$ grains, resulting in $C54\text{-TiSi}_2$ grains as large as $\sim 10\text{--}15\ \mu\text{m}$. An example is illustrated in Fig. 7. Although there is no growth velocity data available, it is expected that these incoherent interfaces have large mobility and are able to migrate very fast under certain circumstances. Within the $C54$ grains, transformation twins were formed to accommodate the strain energy caused by the volume change ($\sim 6\%$ reduction) associated with the transformation.¹⁸ All these microstructural characteristics described above have much resemblance to the distinguished features of massive transformation outlined by Massalski¹⁹ and more recently reviewed by Menon and Aaronson.²⁰

In the literature regarding the $C49\text{-to-}C54$ polymorphic transformation, it has been suggested by several groups^{9,21,22}

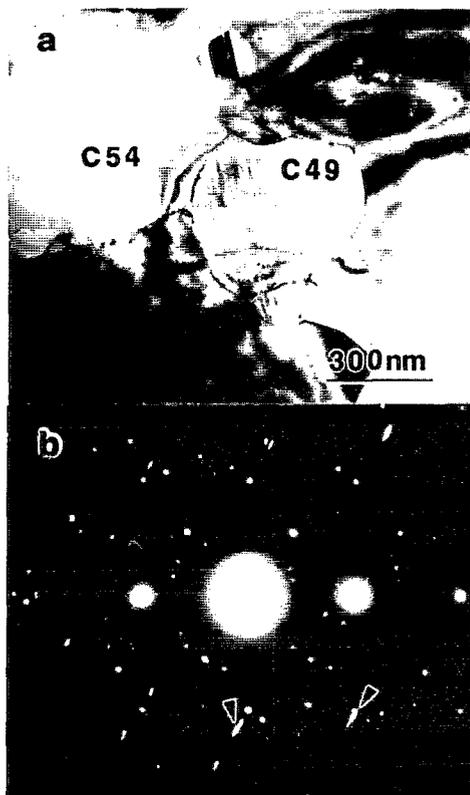


FIG. 5. Typical TEM micrograph taken from a sample after 700 °C, 75 min anneal. The growth front of the C54–TiSi₂ exhibits a ragged appearance, implying its incoherent characteristics. (b) Its corresponding selected area diffraction pattern, confirming the incoherent interface nature. The streaks are due to faulted C49 phase (indicated by arrows).

that this structural transformation proceed via a recrystallization process. If we review the definition for recrystallization,²³ it will be found that this analogy is not appropriate. Recrystallization is referred to those processes where the deformed materials are recovered and crystallized into a relatively defect-free state. This process does not involve a change of crystal structure of the materials. Although the C49-to-C54 phase transformation proceeds by eliminating crystal imperfections in the heavily faulted C49 phase and reconstructing the relatively defect-free C54 phase, the process transforms the disilicide from a base-centered-orthorhombic structure (prototype C49–ZrSi₂) to a face-centered-orthorhombic one (prototype C54–TiSi₂). In this sense, this structural transformation is obviously not a recrystallization process.

Polymorphic transformation is classified as a short-range diffusional transformation, involving local atomic transport across the interphase boundary separating two phases. Two of the possible mechanisms often observed to be operative in polymorphic transformation are *martensitic transformation* and *massive transformation*. The first is a shear type of transformation and is diffusionless. It often exhibits habit planes and rigorous orientation relationships between the parent phase and product phase. The second is a diffusional transformation in which incoherent interfaces advance in all directions by diffusional processes across the interfaces. It is well known that massive transformation often shows no rig-

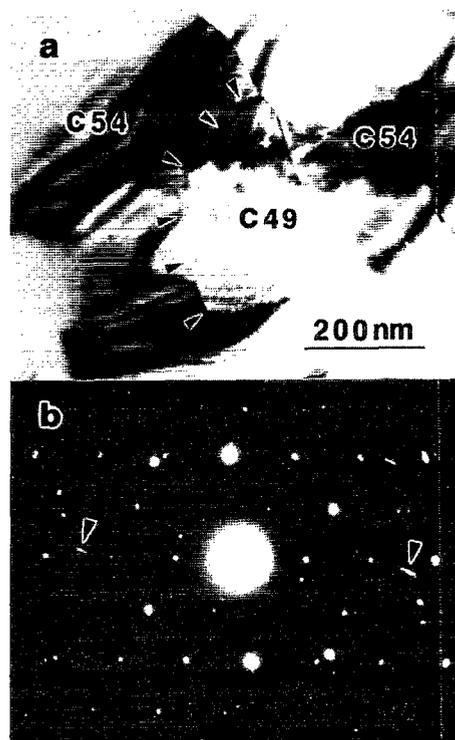


FIG. 6. Typical TEM micrograph taken from the same sample shown in Fig. 5, showing the morphology of the growth front. The growth of the C54 phase proceeds by advancing the mobile incoherent interface toward the C49 phase. A large strain contrast due to the transformation is also seen in the picture. (b) The corresponding selected area diffraction pattern. The streaks are due to the faulted C49 phase.

orous orientation relationships and exhibits explosive growth features.²⁴ From a thermodynamic standpoint, polymorphic transformation may be considered as a limiting case of massive transformation.²⁵ From the main microstructural and morphological data gathered above, we did not observe a martensitic behavior of the transformation. This may also be expected from purely structural analysis of the C49 and C54

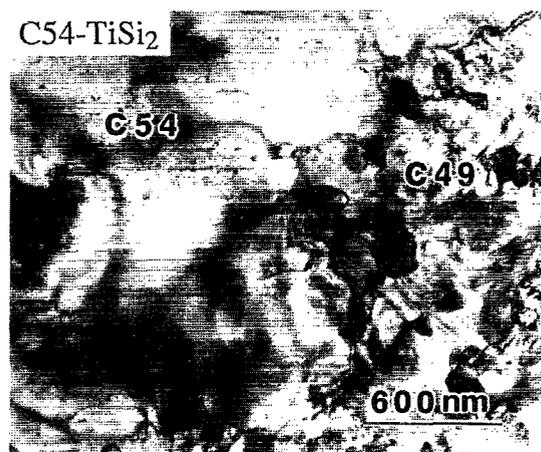


FIG. 7. A typical bright-field TEM micrograph, taken from samples after anneal at 700 °C for about 25 min, showing that some C54–TiSi₂ grains grew across many small C49–TiSi₂ grains by rapidly migrating highly mobile interphase boundaries, resulting in extremely large C54 grains.

disilicides since large mismatches exist between the major crystallographic planes of the two structures, which prevents any shear process from occurring. However, it is noticed that the microstructure and morphology evolved reveal some interesting characteristics resembling those of massive transformation. Both nucleation and growth of the C54 phase reveal some massivelike features. But at this point, no further conclusion can be made on this before any important kinetic parameters such as nucleation and growth rates are established.²⁶

IV. CONCLUSIONS

The microstructural and morphological aspects of the C49-to-C54 polymorphic transformation in titanium disilicide have been investigated with the focus on the nucleation and growth of the C54-TiSi₂. Nucleation of the C54 phase predominantly takes place at triple junctions of the C49 grains with less interphase coherency. No orientation relationships were found between the C49 and C54 phases. The density of triple grain junction nucleation is higher than that of a grain-boundary one. The growth front of the C54 disilicide is highly incoherent. No martensitic characteristics were observed. Both nucleation and growth bear some important microstructural characteristics of massive transformation. Further work on the thermodynamics and detailed kinetic behavior of the transformation is necessary in order to address the mode and more fundamental mechanism of the C49-to-C54 TiSi₂ polymorphic transformation.

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- ¹R. Beyers and R. Sinclair, *J. Appl. Phys.* **57**, 5240 (1985).
- ²*Binary Alloy Phase Diagrams*, edited by T. B. Massalski (ASM International, Materials Park, OH, 1986).
- ³Z. Ma, Y. Xu, L. H. Allen, and S. Lee, *J. Appl. Phys.* **74**, 2954 (1993).
- ⁴A. Kirtikar and R. Sinclair, *Mater. Res. Soc. Symp. Proc.* **260**, 227 (1992).
- ⁵R. D. Thompson, H. Takai, P. A. Psaras, and K. N. Tu, *J. Appl. Phys.* **61**, 540 (1987).
- ⁶L. A. Clevenger, J. M. E. Harper, C. Cabral, Jr., C. Nobili, G. Ottaviani, and R. Mann, *J. Appl. Phys.* **72**, 4978 (1992).
- ⁷R. Beyers, D. Coulman, and P. Merchant, *J. Appl. Phys.* **61**, 5110 (1987).
- ⁸G. Ramanath, S. Koh, Z. Ma, L. H. Allen, and S. Lee, *Mater. Res. Soc. Symp. Proc.* **146**, 267 (1989).
- ⁹X. H. Li, J. R. A. Carlsson, S. F. Gong, and H. T. G. Hentzell, *J. Appl. Phys.* **72**, 514 (1992).
- ¹⁰J. B. Lasky, J. S. Nakos, O. J. Cain, and P. J. Geiss, *IEEE Trans. Electron Devices* **ED-34**, 575 (1990).
- ¹¹Y. Matsumura, T. Horiuchi, and K. Okumura, *Appl. Phys. Lett.* **62**, 2634 (1993).
- ¹²L. H. Allen, G. Ramanath, S. Lai, Z. Ma, S. Lee, D. D. J. Allman, and K. P. Fuchs, *Appl. Phys. Lett.* **64**, 417 (1994).
- ¹³A. Bourret, F. M. d'Heurle, and A. Charai, *J. Appl. Phys.* **67**, 241 (1990).
- ¹⁴C. L. Jia, J. Jiang, and X. F. Zong, *Philos. Mag. A* **59**, 999 (1989).
- ¹⁵D. A. Porter and K. E. Easterling, *Phase Transformations in Metals and Alloys* (VNR International, England, 1988).
- ¹⁶P. M. Robinson and M. B. Bever, in *Intermetallic Compounds*, edited by J. H. Westbrook (Wiley, New York, 1967), p. 38.
- ¹⁷P. J. Clemm and J. C. Fisher, *Acta Metall.* **3**, 70 (1955).
- ¹⁸K. Rajan, *Metall. Trans. A* **21**, 2317 (1990).
- ¹⁹T. B. Massalski, *Metall. Trans. A* **15**, 421 (1984).
- ²⁰E. S. K. Menon and H. I. Aaronson, *Mater. Sci. Forum* **3**, 211 (1985).
- ²¹H. J. W. van Houtum and I. J. M. M. Raaijmakers, *Mater. Res. Soc. Symp. Proc.* **54**, 37 (1986).
- ²²H. J. W. van Houtum, I. J. M. M. Raaijmakers, and T. J. M. Menting, *J. Appl. Phys.* **61**, 3116 (1987).
- ²³*Recrystallization '90*, edited by T. Chandra (The Minerals, Metals, Materials, Warrendale, PA, 1990).
- ²⁴T. B. Massalski, in *Phase Transformations* (ASM, Metals Park, OH, 1970), p. 433.
- ²⁵A. K. Jena and M. C. Chaturvedi, *Phase Transformations in Materials* (Prentice-Hall, Englewood Cliffs, NJ, 1992).
- ²⁶Z. Ma and L. H. Allen, *Phys. Rev. B* **49**, 13501 (1994).