Evaluation of Al(Nd)-alloy films for application to thin-film-transistor liquid crystal displays

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Higher-resolution, larger-diagonal active-matrix liquid crystal displays (AMLCDs) will require the use of low-resistivity gate metal such as aluminum transition-metal alloys. Al(Nd ≧ 3 wt.%) alloy films are adequate for AMLCD fabrication because of their low resistivity and their tendency not to form hillocks during thermal processing. The use of both optical light scattering and nanoindentation for the rapid evaluation of hillock formation has been demonstrated, along with the use of ramped resistance measurements for observing the process of discontinuous precipitation (the combination of Al grain growth and Al–Nd compound precipitation). Al(Nd) films were further characterized by TEM and AFM to confirm the effect of their finely dispersed Al–Nd compound precipitates on decreased grain size and decreased hillock formation.

Introduction

Since the early 1980s, the size and complexity of AMLCDs have increased dramatically, with a projected market value of 7–15 billion dollars in the year 2000 [1]. These trends are expected to continue, with increased penetration into the desktop display market [2]. Scaling analysis [1] has shown that lower-resistivity gate metals, such as Al alloys, will be required for larger, higher-resolution displays. Unlike the refractory metals or alloys currently used, the thermal expansion mismatch between Al films and the glass substrate of an AMLCD can result in the formation of hillocks [3, 4] and/or whiskers [5] during display fabrication. Whisker formation occurs when grain growth is suppressed during heat treatment of Al films, causing localization of the stress relief [5]. Alloying Al films with transition metals can minimize hillock or whisker formation [6–9].

Key requirements for gate-line materials for TFT/LCD arrays are low resistivity (≦5 $\mu\Omega$-cm), resistance to stress migration (no formation of hillocks or whiskers), good adhesion to glass, and the ability to be patterned with a

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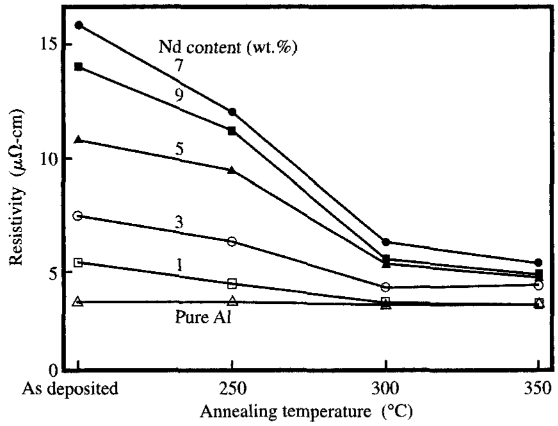

Figure 1

Resistivity vs. isothermal annealing temperature for pure Al films and Al(1–9 wt.% Nd)-alloy films. The Al(Nd) films were 215–235 nm thick and the Al films were 220 nm thick. Annealing was carried out for 20 min.

tapered edge by wet or dry etching. A comparison of gate-line materials is shown in **Table 1**. The formation of a tapered edge is important to ensure adequate coverage by the gate insulator and subsequent metal layers. Thermal processing causes Al grain growth and precipitation of an Al–transition-metal compound at grain boundaries; this reduces the resistivity of the Al-alloy films. The initial resistivity of Al-alloy films is higher than that of pure Al films because sputter deposition can form nonequilibrium solid solutions with an amorphous or very fine grain structure. When the Al grains grow, the recrystallization front sweeps the alloy additions out of the grains to form precipitates at the grain boundaries, in a process referred to as "discontinuous precipitation" [10]. If the alloy addition has a very limited solubility (0.008 at.% Nd in Al at 640°C [11]), the annealed resistivity is much lower than the as-deposited resistivity because of decreased solute scattering. The final resistivity after annealing is higher than that of pure Al films, primarily because of the reduction in Al grain size and the presence of precipitate particles at the grain boundaries. The formation of hillocks or whiskers usually occurs when the room-temperature glass plate with patterned gate metal is transferred onto a heated chuck (>300°C) before chemical vapor deposition of the gate insulator film.

The relationships among resistivity, microstructure, and hillock or whisker formation in Al films containing between 0 and 10 wt.% Nd on glass have been studied. The film properties were characterized using resistance measurements, tapping-mode atomic force microscopy (AFM), transmission electron microscopy (TEM), optical scattering, and nanoindentation. Optical scattering and nanoindentation provide rapid means of evaluating hillock formation without tedious microscopic examination.

The Al(Nd) samples were deposited by sputtering from alloy targets on BaO–BO–SiO glass (Corning 7059) substrates (thermal coefficient of expansion of 5 ppm/°C vs. 24 ppm/°C for Al). Films with a range of compositions (0, 1, 3, 5, 7, and 9 nominal wt.% Nd) were deposited on 5-in.-square substrates at a rate of about 180 nm/min, at an argon pressure of 0.4 Pa and a substrate temperature of 120°C by means of a dc fixed-magnetron sputtering apparatus. Films with a nominal composition of 10 wt.% Nd were deposited on 300 × 400-mm substrates by a scanning magnet dc magnetron sputtering apparatus at a rate of about 300 nm/min, at an argon pressure of 0.4 Pa and a substrate temperature of 120°C. The film thicknesses, as measured by Rutherford backscattering spectrometry, ranged from 215 to 235 nm for the films prepared on small substrates and were 295 nm for the films prepared on the large substrates. The optical scattering measurements were performed simultaneously with resistance measurements *in situ* during heating at 180°C/min in nitrogen [12]. For the geometry used, the optical scattering was sensitive to lateral length scales of 0.5 μm. The amount of optical scattering increases when the film surface roughness increases and hillocks form. Since the film resistivity depends on the microstructure,

Table 1 Gate-line materials for TFT/LCD arrays.

Material	*Resistivity* ($\mu\Omega$-cm)	*Stress migration resistance*	*Adhesion to glass substrate*	*Taper etching ability*
MoTa	40	Good	Fair	Good
MoW	15	Good	Fair	Fair
Al alloy (transition metal)	after annealing, 4–6	Good	Good	Good
Al–Cu	3–3.5	Fair	Good	Good
Pure Al	2.7	Poor	Good	Good
Cu	2.0	Good	Poor	Fair

ramped resistance measurements were used to determine the apparent activation energy for discontinuous precipitation [13]. For nanoindentation measurements, indentation marks were made at regular intervals on the films using a Vickers hardness tester. The samples were then rapidly heated to 300°C in vacuum, held at that temperature for 80 minutes, and slowly cooled. The indentation marks were then inspected for the formation of hillocks and/or whiskers [14].

Results and discussion

With isothermal annealing, the resistivity of Al(Nd) films decreases sharply between 250°C and 300°C, as shown in **Figure 1**. The as-deposited resistivity increased with the Nd content. After annealing at 350°C for 20 min, the resistivity ranged from 3.6 to 5.4 $\mu\Omega$-cm. This decrease in resistance on annealing corresponds to discontinuous precipitation, during which the Al grains grow and Al–Nd precipitate particles form at the grain boundaries, as shown in **Figure 2**. The faint layered structure in the as-deposited film [Figure 2(a)] resulted from the multiple scans during deposition. Annealing [Figure 2(b)] resulted in the formation of fine vertically oriented Al grains with Al–Nd precipitates at the grain boundaries. The evolution of surface roughness (area mean, Ra) with annealing and Nd content was measured by AFM (**Figure 3**). Representative AFM images of the as-deposited and annealed pure Al and Al(5 wt.% Nd) films are also shown in Figure 3. The largest change in surface roughness during annealing occurs for the pure Al film, and there is no significant change in roughness with annealing at up to 350°C for the Al(≧3 wt.% Nd) alloy films. The Al(1 wt.% Nd) films were significantly rougher than the more Nd-rich films and were almost as rough as the pure Al films after annealing.

Resistivity and optical scattering were measured during heating at 180°C/min to 600°C for pure Al films and various Al(Nd) film compositions, as indicated in **Figure 4**. Note that the Al(10 wt.% Nd) film was deposited on a large substrate in a scanning system using different deposition conditions. The resistivity of the Al(Nd) alloys decreased markedly at about 330°C [Figure 4(a)]. This is a higher temperature for discontinuous precipitation than with isothermal annealing (Figure 1), as expected for ramped annealing. The optical scattering [Figure 4(b)] increased for the pure Al films starting at 200°C compared to no increase in scattering for the Al(Nd) films until above 400°C. Although the temperatures are well beyond those of interest, the optical scattering increased less at temperatures between 400°C and 600°C for the Al(Nd) films having the highest Nd content. The results for the Al(10 wt.% Nd) films were consistent with results for the other films, suggesting that the evolution of the microstructure with annealing was unaffected by the initial

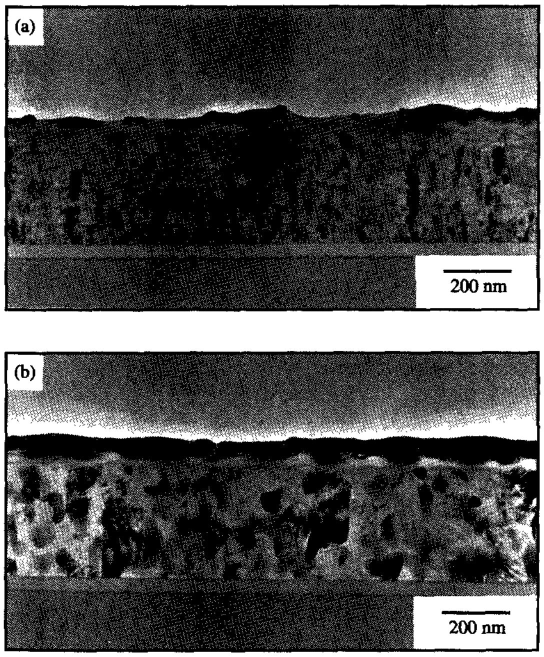

Figure 2

TEM cross sections of an Al(10 wt.% Nd) film on glass coated with an SiO layer (a), and after annealing in vacuum at 300°C for one hour (b).

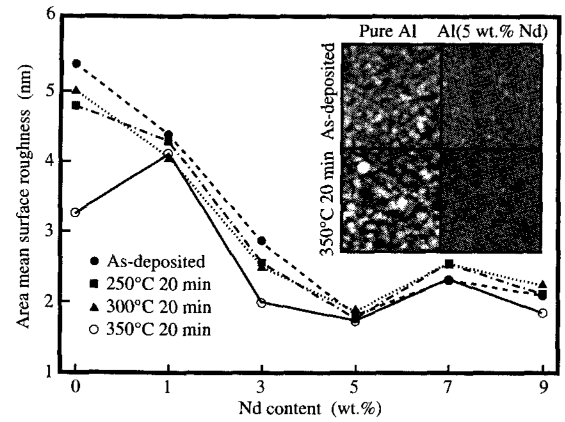

Figure 3

Area mean surface roughness (Ra) vs. 0–9 wt.% Nd content for various heat treatments measured by an atomic force microscope (AFM). AFM images are shown for a pure Al film and for an Al(5 wt.% Nd) film. The area of each image is 2 μm × 2 μm, with a vertical scale of 100 nm.

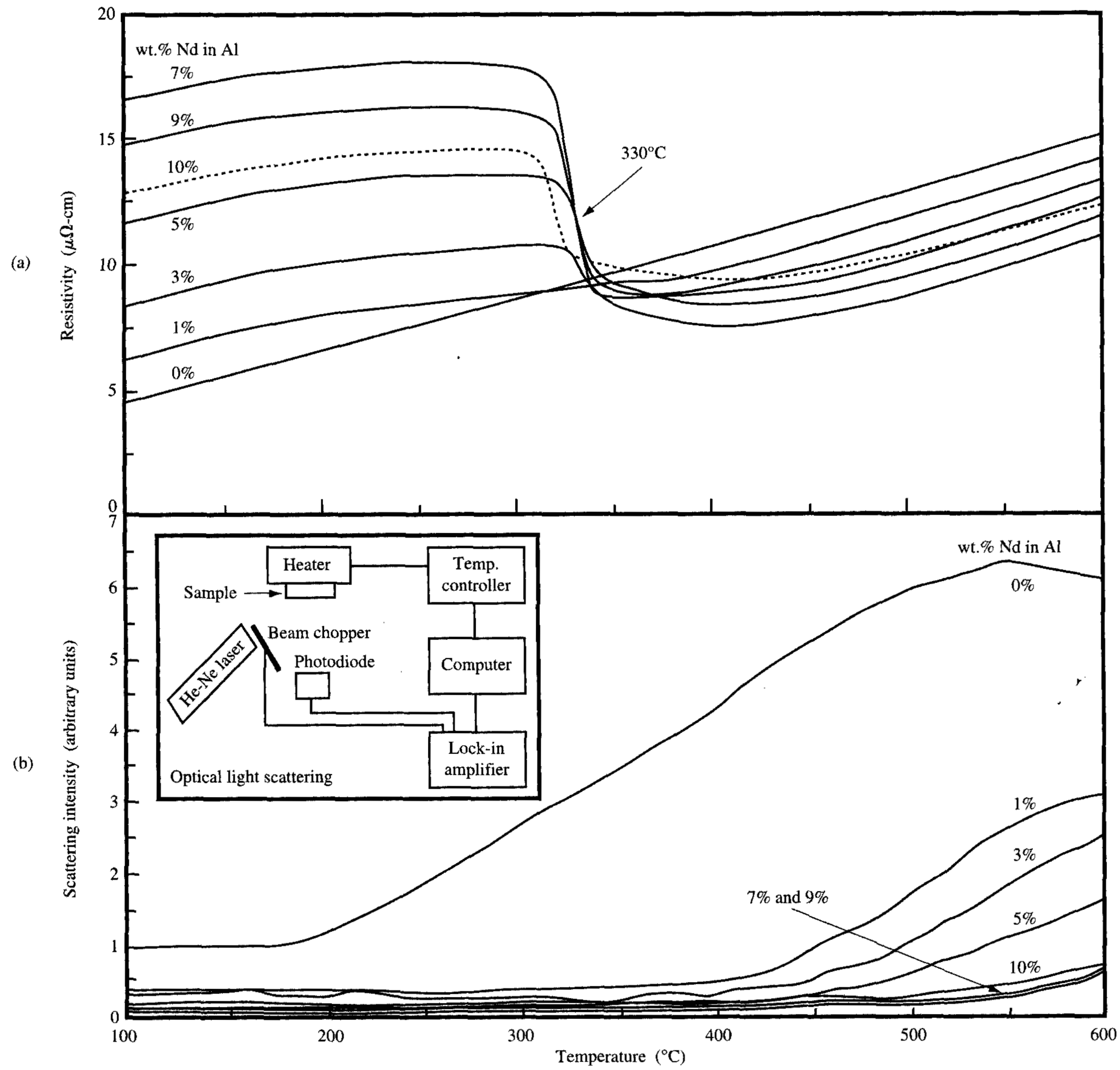

Figure 4

Resistivity (a) and scattering intensity (b) during heating at 180°C/min to 600°C for pure Al and the indicated Al(1–10 wt.% Nd) alloys. Insert shows the experimental setup used for measuring the scattered light intensity during heating.

layered structure (Figure 2). For a temperature of 350°C, the scattered intensity was greatest for the pure Al films and next greatest for the Al(1 wt.% Nd) films, which is consistent with the AFM surface roughness measurements in Figure 3 obtained after annealing. Measurements on Al(Cu) films (not shown) indicated increasing scattering for temperatures above 300°C.

Further ramped resistivity measurements at heating rates between 1°C and 180°C/min for the Al(1, 5, or 9 wt.% Nd) films are plotted in **Figures 5(a)–(c)**. With increased ramp rates, the discontinuous precipitation temperature shifted to higher temperatures, indicating that it is a thermally activated process. The resistivity of the Al(1 wt.% Nd) films decreased significantly during heating before discontinuous precipitation occurred, especially for the lowest heating rates. The resistivity of the Al(5 or 9 wt.% Nd) films changed only slightly during heating prior to discontinuous precipitation. Assuming a direct correlation between the film microstructure and resistivity, this suggests that the grain growth and/or Al–Nd precipitation is not delayed as effectively by the addition of 1 wt.% Nd as by the addition of 5 or 9 wt.% Nd. The abrupt change in resistivity for the Al(5 or 9 wt.% Nd) suggests that the relatively large stored energy for Al grain growth and the stored energy for Al–Nd precipitate formation are released at the same time.

Several driving forces, or sources of stored energy, are available to drive the microstructure evolution in sputtered Al(Nd)-alloy films during annealing [15]. First, the supersaturated solution of Nd atoms in Al is precipitated, releasing the heat of solution. Second, the formation of Al–Nd compound precipitates releases the heat of reaction. Third, grain growth releases energy by the elimination of grain-boundary area. These three mechanisms are coupled in such a way that they occur abruptly in a narrow temperature range upon heating.

The shift in discontinuous precipitation temperature with ramp rate can be used to determine an apparent activation energy for the overall process through a Kissinger-like method [13, 16, 17]. In the Kissinger analysis, the dependence of transformation temperature on ramp rate is used to determine a single activation energy. The measured apparent activation energies were thus found to be nearly identical for the different Al(Nd) films, with a value of 2.1 to 2.2 eV. While the discontinuous precipitation process cannot be described with a single mechanism, this value of apparent activation energy is useful in predicting the temperature of precipitation at other ramp rates. The temperature for discontinuous precipitation, at a given ramp rate, was on average 22°C higher for the Al(1 wt.% Nd) films than for the Al(5 wt.% Nd) films. The shift to higher temperatures for the Al(1 wt.% Nd) films is likely the result of some initial grain growth and/or Al–Nd precipitation, as evidenced by the reduced resistance, prior to the abrupt discontinuous precipitation, which reduced the thermodynamic driving force for discontinuous precipitation.

These apparent activation energies can be compared to results from similar measurements on Al(Cu) films [13] in which, for Al(2 or 4 wt.% Cu) films between 0.5 and 2 μm thick, the apparent activation energy for discontinuous precipitation (Al_2Cu precipitation) ranged from 1.2 to 1.4 eV for blanket films and from 1.9 to 3.1 eV for patterned lines 1 μm thick and about 0.65 μm wide. The discontinuous precipitation in the patterned lines took place at temperatures approximately 200°C higher than in corresponding blanket films, in which discontinuous precipitation occurred between 90°C and 155°C. The differences in the behavior of blanket and patterned lines

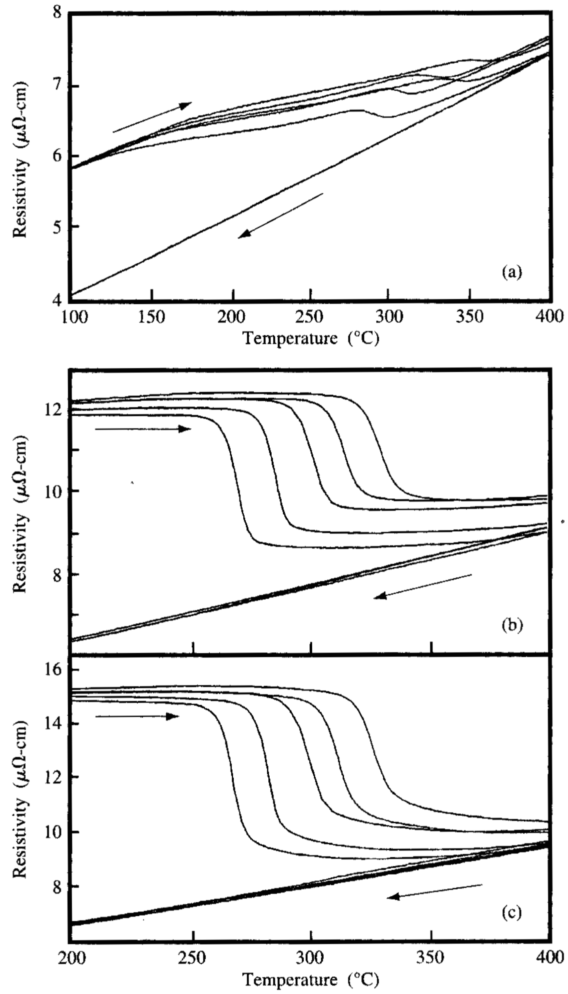

Figure 5

Resistivity vs. temperature for an Al(1 wt.% Nd) film (a); for an Al(5 wt.% Nd) film (b); and for an Al(9 wt.% Nd) film (c) for ramp rates from 1°C to 180°C/min.

were attributed to the constraints on grain growth and nucleation in the patterned lines. The addition of a refractory metal alloying element by sputtering retards the Al grain growth in a somewhat analogous manner. The recrystallization front is hindered not by geometry, but by the need to displace the refractory metal atoms. The presence of Nd greatly increases the temperature at which grain growth occurs, reducing the grain size. The temperature at which discontinuous precipitation occurs is important, because it has been found that for Al alloyed with transition metals, the compressive stress caused by the thermal expansion mismatch between the Al-alloy film and its glass substrate is abruptly reduced to a near-zero

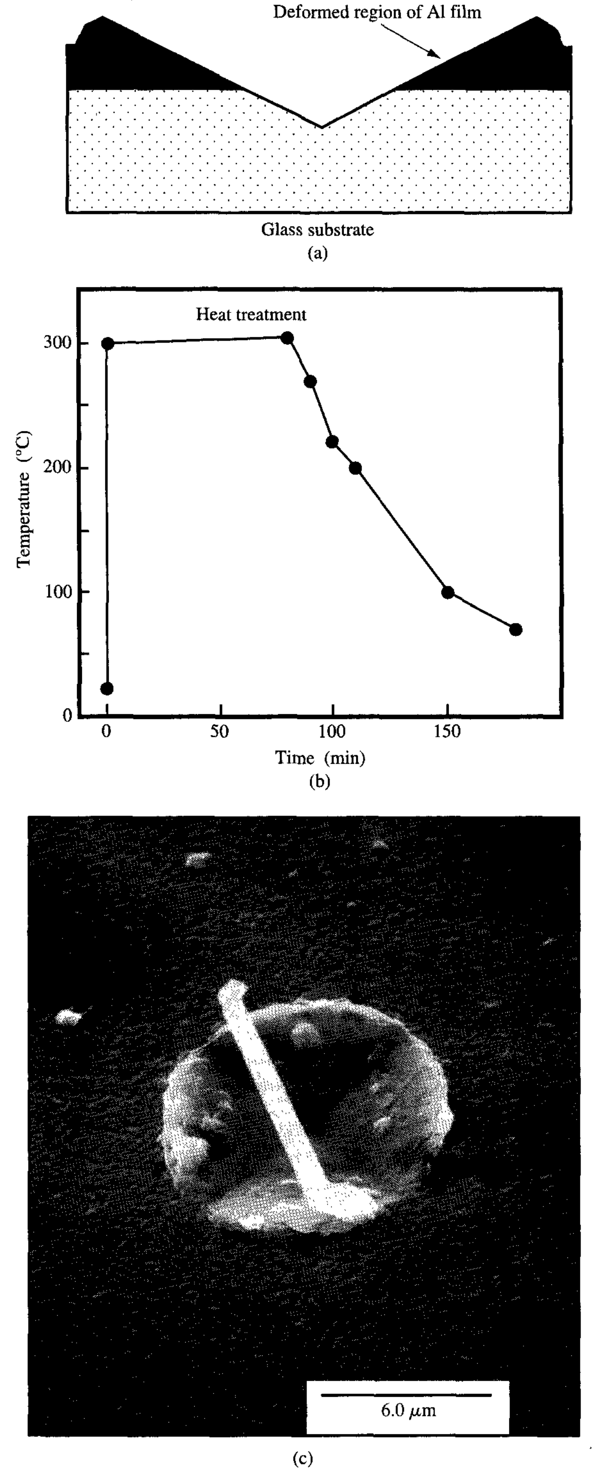

Figure 6

Schematics of (a) nanoindentation technique and (b) heat treatment used; (c) SEM micrograph of a pure Al film showing a whisker and hillock formed by nanoindentation and annealing.

value by Al grain growth and precipitation [9]. The reduction in grain size, especially avoiding columnar grains through the thickness of the film, allows any further stress relief to be accommodated by intergranular sliding or localized grain deformation rather than by large-scale deformation, which can lead to the formation of hillocks and/or whiskers.

The nanoindentation technique, which was previously applied to pure Al and Al(0.2 wt.% Cu) films [14], has been found to be a rapid and accurate means for characterization of stress migration. Additionally, it has been found that whisker generation correlates strongly with the crystallographic texture of the films. The conventional methods required patterned metal layers and exhaustive microscopic examination to detect hillocks or whiskers after annealing. The nanoindentation technique consists of making an array of indentations in the film by means of a Vickers hardness tester [**Figure 6(a)**] rapidly heating the sample, maintaining it at temperature in vacuum [**Figure 6(b)**], and then inspecting the indentation sites for hillock and/or whisker formation [**Figure 6(c)**]. A consistent indentation depth and heating rate are important for comparisons between films. The results of the nanoindentation measurements were as follows: 31 hillocks and four whiskers appeared on the pure Al film; six hillocks and no whiskers appeared on the Al(1 wt.% Nd) film; and no hillocks or whiskers appeared on the remaining Al(Nd) films. These results confirm the effectiveness of adding Nd to Al for suppressing the growth of hillocks and whiskers, and are consistent with results obtained by the rapid measurements of resistivity and optical scattering.

Summary

The resistivity and stress migration properties of Al(Nd $\geqq$ 3 wt.%)-alloy films are adequate for AMLCD fabrication. The use of optical scattering and nanoindentation for the rapid evaluation of hillock formation has been demonstrated. The apparent activation energy for discontinuous precipitation (the combination of Al grain growth and Al–Nd compound precipitation) was determined using ramped resistance measurements and ranged from 2.1 to 2.2 eV for the Al(1, 5, or 9 wt.% Nd) films.

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References

1. W. E. Howard, "Limitations and Prospects of a-Si:H TFTs," *J. SID* **3,** No. 3, 127 (1995).
2. W. C. O'Mara, "If You Want a Bigger FPD, Use a Bigger Substrate," *Solid State Technol.* **39,** No. 7, 76–83 (July 1996).
3. P. Chaudhari, "Hillock Growth in Thin Films," *J. Appl. Phys.* **45,** 4339 (1974).
4. F. Ericson, N. Kristensen, J.-A. Schweitz, and U. Smith, "A Transmission Electron Microscopy Study of Hillocks in Thin Aluminum Films," *J. Vac. Sci. Technol. B* **9,** No. 1, 58 (1991).
5. K. Hinode, Y. Homma, and Y. Sasaki, "Whiskers Grown on Aluminum Thin Films During Heat Treatments," *J. Vac. Sci. Technol. A* **14,** No. 4, 2570 (1996).
6. Y. K. Lee, N. Fujimura, T. Ito, and N. Nishida, "Annealing Behavior of Al–Y Alloy Film for Interconnection Conductor in Microelectronic Devices," *J. Vac. Sci. Technol. B* **9,** No. 5, 2542 (1991).
7. S. Takayama and N. Tsutsui, "Low Resistivity Al RE (RE = La, Pr, and Nd) Alloy Thin Films with High Thermal Stability for Thin Film Transistor Interconnects," *J. Vac. Sci. Technol. B* **15,** No. 5, 3257 (1996).
8. S. Takayama and N. Tsutsui, "Effects of Y or Gd Additions on the Structure and Resistivity of Al Thin Films," *J. Vac. Sci. Technol. A* **14,** No. 4, 2499 (1996).
9. T. Onishi, E. Iwamura, K. Takagi, and K. Yoshikawa, "Influence of Adding Transition Metal Elements to Aluminum Target on Electrical Resistivity and Hillock Resistance in Sputter-Deposited Aluminum Alloy Thin Films," *J. Vac. Sci. Technol. A* **14,** No. 5, 2728 (1996).
10. E. Hornbogen and U. Koster, in *Recrystallization of Metallic Materials*, F. Haessner, Ed., Dr. Riederer Verlag GmbH, Stuttgart, Germany, 1978, Chapter 8.
11. *Binary Alloy Phase Diagrams*, T. B. Massalski, Ed., ASM International, Materials Park, OH, 1990.
12. C. Lavoie, C. Cabral, Jr., L. A. Clevenger, J. M. E. Harper, J. Jordan-Sweet, K. L. Saenger, and F. Doany, "Light Scattering Measurement of Surface Topography During Formation of Titanium Silicide," *Mater. Res. Soc. Symp. Proc.* **406,** 163 (1996).
13. E. G. Colgan, K. P. Rodbell, C. Cabral, Jr., and J. M. E. Harper, "Kinetics of Al Grain Growth, AlCu Precipitation, and Dissolution in Blanket Thin Films and Fine Lines," *J. Appl. Phys.* **76,** No. 5, 2781 (1994).
14. H. Takatsuji, S. Tsuji, H. Kitahara, K. Tsujimoto, K. Kuroda, and H. Sako, "Nanocharacterization of Texture and Hillock Formation in Thin Al and Al–0.2% Cu Films for Thin-Film Transistors," *Proceedings of the Symposium on Thin Films—Structure and Morphology*, Boston, December 2–6, 1996, pp. 415–420.
15. J. M. E. Harper and K. P. Rodbell, "Microstructure Control in Semiconductor Metallizations," *J. Vac. Sci. Technol. B* **15,** No. 4, 763–779 (1997).
16. E. J. Mittermeijer, A. Van Gent, and P. J. Van der Schaaf, "Analysis of Transformation Kinetics by Nonisothermal Dilatometry," *Metall. Trans.* **A17,** 1441 (1986).
17. E. J. Mittermeijer, L. Cheng, P. J. Van der Schaaf, C. M. Brakman, and B. M. Korevaar, "Analysis of Nonisothermal Transformation Kinetics; Tempering of Iron–Carbon and Iron–Nitrogen Martensites," *Metall. Trans.* **A19,** 925 (1988).

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