Vapor phase growth of Al whiskers induced by glancing angle deposition at high temperature

Motofumi Suzuki,[a)] Koji Nagai, Sadamu Kinoshita, Kaoru Nakajima, and Kenji Kimura
Department of Micro Engineering, Kyoto University, Kyoto 606-8501, Japan

Tomoki Okano and Kaoru Sasakawa
KOBELCO Research Institute, Inc., 1-5-5 Takatsukadai, Nishi-ku, Kobe 651-2271, Japan

(Received 8 July 2006; accepted 1 August 2006; published online 25 September 2006)

The authors demonstrate the growth of unusual Al whiskers by glancing angle deposition on a high temperature (HT-GLAD) substrate, while the usual columnar structures completely disappear due to accelerated surface diffusion. HT-GLAD is essential for the nucleation of the whiskers and efficient supply of Al atoms on the side surface of the vertically growing whiskers. HT-GLAD will, for the first time, reveal the mechanisms for the vapor growth of metal whiskers. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2357582]

Growth kinetics and morphology of various nanocrystalline materials such as thin epitaxial films, nanorods, nanowires, and nanoparticles are explained within a framework of the crystal growth theory developed by Burton *et al.*[1] in the 1950s. Generally, in order to obtain a high quality crystal, it is important to enhance the surface diffusion of adatoms and increase the probability of reaching a stable site. Therefore, researchers who investigate nanocrystalline materials do not focus heavily on the relation between the traveling direction of atoms before impingement and the morphology of the resulting crystals.

On the other hand, the directivity of incident atoms strongly influences the morphology of films prepared under low surface diffusivity. It is well known that oblique columns grow in the direction of the incident vapor beam due to the self-shadowing effect, when vapor flux is incident obliquely. Since the end of the 1980s, many efforts have been made to control the thin film morphology by oblique deposition.[2–6] In order to obtain unique morphologies, it is crucial to control the directivity of the incident vapor, while surface diffusion is considered to be a problem for columnar growth.

Recently, it has been reported that columnar films with unique crystallinity can be created by oblique deposition at a high deposition angle [glancing angle deposition (GLAD)] when surface diffusion is rather significant.[7–9] However, even in these studies, the self-shadowing effect is dominant and therefore the fundamental columnar structures are retained. In the present study, we investigate Al films prepared by high temperature glancing angle deposition (HT-GLAD) in which surface diffusion is so significant that the usual columnar growth due to the self-shadowing effect is prohibited. We have found that two types of whiskers grow only under HT-GLAD conditions, although the usual columnar structures disappear.

Aluminum (purity 99.999%) was deposited on a surface-oxidized Si substrate in an electron-beam (EB) evaporation apparatus specially designed for HT-GLAD. After evacuating the preparation chamber to 1×10^{-4} Pa, the substrate set on a graphite plate was irradiated with a halogen lamp to heat substrate. The relation between the substrate temperature measured on the graphite plate by thermocouples and that of the halogen lamp was calibrated by the preliminary experiments. In the present work, the substrate temperature was maintained constant at (400 ± 10) °C during the deposition by monitoring the temperature of the halogen lamp. In order to reduce the dispersion of the deposition flux of Al, the EB source was located at a distance of 480 mm from the center of the substrate. The deposition angle α, which is defined as the angle between the substrate normal and the incident direction of the deposition flux, was set between 58° and 85° by using an in-vacuum stepper motor. The thickness $d(\alpha)=d_0\cos\alpha$ and deposition rate $\dot{d}(\alpha)=\dot{d}_0\cos\alpha$ were monitored by a quartz crystal monitor such that they were almost constant at $d(\alpha)=72$ nm and $\dot{d}(\alpha)=0.5$ nm/s, where d_0 and $\dot{d}_0$ are the thickness and deposition rate calibrated for films deposited from the normal direction at room temperature, respectively. The pressure during the deposition was less than 4×10^{-4} Pa. The samples were characterized by a transmission electron microscope (TEM) equipped with an energy dispersive x-ray detector, scanning electron microscope (SEM).

Figure 1 shows the SEM images of a cross section of the samples fractured parallel to the plane of incidence of the Al vapor flux. In all samples, usual oblique columnar structures are not observed. Instead, sparsely distributed whiskers, which have a rodlike shape (nanorods) with a thickness of approximately 500 nm or a wirelike shape (nanowire) with a thickness of less than 100 nm, exist on the sample deposited at $\alpha=85°$, as shown in Fig. 1(a). The thin nanowires are also found on the sample prepared at $\alpha=73°$, while no nanorods are found [Fig. 1(b)]. However, neither nanorods nor nanowires are found on the sample deposited at $\alpha=58°$ [Fig. 1(c)]. We have confirmed that these whiskers grow at a temperature above 300 °C, and no significant impurities are detected in the whiskers.

Most of the nanorods have a similar thickness of 560 ± 80 nm and their lengths are 3–4, 1.5, and 1.0 μm. Few nanorods have an intermediate size. Figure 2 shows the detailed morphology of the nanorods and nanowires on the sample prepared at $\alpha=85°$. Figures 2(a) and 2(b) show the magnified images of the nanorods indicated by an asterisk in Fig. 1(a). Evidently, both nanorods are bounded by facets parallel to their axis. The number of facets that bound each

[a)]Electronic mail: m-snki@mbox.kudpc.kyoto-u.ac.jp

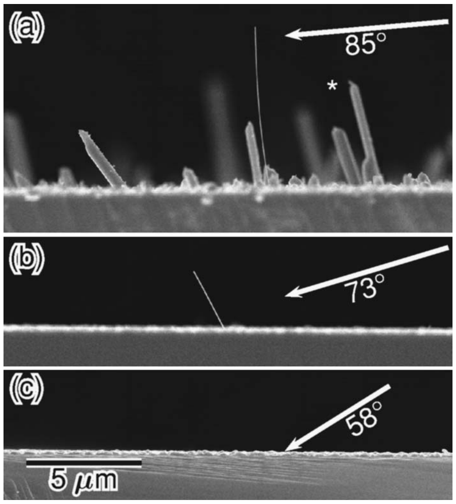

FIG. 1. SEM images of cross section of Al films deposited on the substrate maintained at 400 °C at deposition angles of (a) 85°, (b) 73°, and (c) 58°. The arrows indicate the incident direction of Al vapor. Magnified images of the nanorods indicated by an asterisk are shown in Fig. 2.

nanorod is different. In many nanorods, fine particles are observed on the side surface that is directly exposed to the Al vapor, as in the case of the right nanorod in Figs. 2(a) and 2(b). In contrast, some nanorods have a smooth side surface, as in the case of the left nanorod in Figs. 2(a) and 2(b). A small number of nanorods have an abacuslike shape, as shown in Fig. 2(c). The variation in the shape of the nanorods suggests the occurrence of changes in crystallinity. The TEM observations indicate that these nanorods contain some defects and the axial crystallographic orientation has not yet

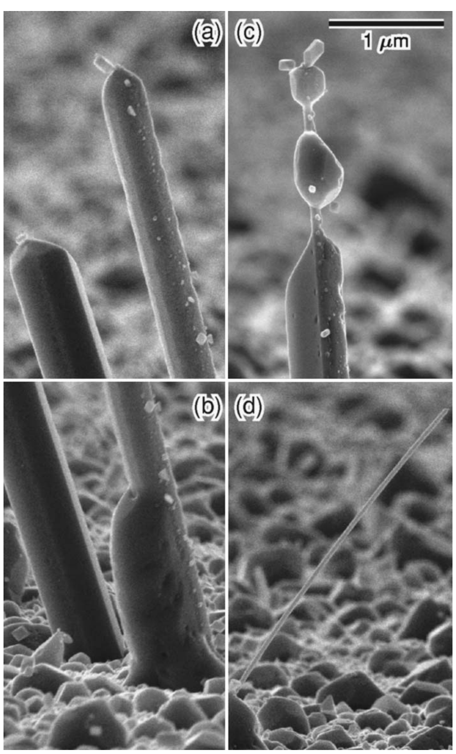

FIG. 2. SEM images of [(a)–(c)] nanorods and (d) nanowires of Al. (a) and (b) show magnified images of the nanorods indicated by an asterisk in Fig. 1(a). The images shown in (c) and (d) were obtained in a region different from that shown in Fig. 1(a) in the same sample. The incident direction of Al vapor was from the right to the left.

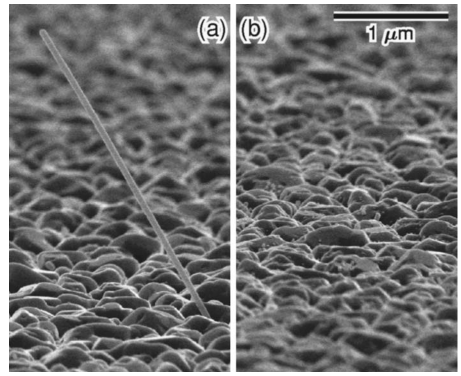

FIG. 3. SEM images of samples deposited at (a) $\alpha=73°$ and (b) $\alpha=58°$.

been determined. Detailed analysis of the crystallographic structures of the nanorods will be performed in future study.

On the other hand, the thickness of the nanowires found on the films deposited at $\alpha=85°$ and 73° is significantly less than that of the nanorods. For example, the full width of nanowires in Figs. 1(a), 1(b) [see also Figs. 3(a)] and 2(d)] is 50 ± 5 nm, while their lengths are 7.1, 3.0, and 3.0 μm, respectively. Although the thickness of all other nanowires is approximately 50 nm, their length is in the range of a few 100 nm to sub-10 μm. In contrast to the nanorods, the nanowires neither contain fine particles on their side face nor have any facets. Since the SEM and TEM observations are conducted *ex situ*, oxidation in the atmosphere might eliminate the facets. In fact, by using the TEM, we have confirmed that the core of the nanowires is ⟨110⟩-oriented single crystalline Al and approximately 5 nm of their side surface is oxidized. In contrast to the case of the nanorods, no significant defects are observed in the nanowires.

On the sample preared at $\alpha=85°$, there are many faceted grains around the bases of the nanorods, as shown in Figs. 2(b) and 2(d). Their facets are oriented in random directions. Some of these grains whose structure is appropriate for rapid axial growth may be nucleated and grow into nanorods. On the other hand, Fig. 3 shows the SEM images of the surface of the films deposited at $\alpha=73°$ and 58°. In both cases, rough granular surfaces are created and the grains have facets. However, the grain morphology of these samples is significantly less sharper than that of the sample prepared at $\alpha=85°$. These differences in the surface morpohology suggest that the self-shadowing in HT-GLAD siginificantly influences the nucleation process of the whiskers.

The first Al whiskers were grown on a hot tungsten wire[10] and a wall of a ceramic crucible[11] from pure Al vapor. However, there are few reports on the vapor growth of Al whiskers on a flat substrate, although it is possible to achieve the solid phase growth of Al whiskers on the flat substrate by electromigration[12,13] or stress-induced migration.[14,15] In these studies, it is reported that the whiskers are not grown on as-deposited films on a hot substrate. Although the previous reports appear to be somewhat inconsistent with each other, it should be noted that during the deposition on the tungsten wire or the crucible wall, a significant amount of Al atoms can be incident on the substrate from the oblique direction. The present study demonstrates that the oblique incidence of the vapor plays an important role in whisker formation.

For the vapor phase growth of metal whiskers, Sears[16] and Melmed and Gomer[10] have proposed a growth mechanism that involves the diffusion of adatoms over the whisker sides, followed by incorporation on the top of the whiskers. In this model, the surface diffusion length of adatoms must be significantly greater than the radius of the whiskers. In the case of the nanorods and nanowires observed in this study, the form anisotropy in the radial direction is not very strong, irrespective of the unidirectional incidence of the Al vapor. This suggests that the surface diffusion length of Al adatoms is significantly larger than the radius of the nanorods and nanowires. By assuming that all atoms impinging upon the whiskers are incorporated and their radius does not change during the growth,[10,16] the length of the whiskers is expressed in the exponential form as $l(d)=l_0 \exp(\gamma d)$, where

$$\gamma=\frac{2\tan\alpha}{\pi r}, \tag{1}$$

and r is the radius of the nanorod or nanowire. In the case of the nanorods grown at $\alpha=85°$, $d=72$ nm, $r=250$ nm, and $l(d)=4$ μm such that $l_0 \approx 500$ nm. Therefore, considerably tall seeds must exist even at the beginning of the nanorod growth. This indicates that the significant amount of Al atoms deposited on the film/substrate surface as well as those on the side surface of the whiskers contribute to the nanorod growth. The surface diffusion length on the film surface is also long since no significant anisotropy is observed for the granular morphology of the surface. Moreover, we have confirmed that nanorods with a length of almost 1 μm already exist on the sample with $d=8$ nm deposited at 300 °C. It is certain that Al atoms deposited on the film surface at $\alpha=85°$ significantly contribute to the growth of the nanorods.

On the other hand, the nanowires can be grown from the tiny nucleus only by the incorporation of atoms impinging upon their sides. Even at $\alpha=73°$, the height of the nucleus required for the nanowires with a length of 3 μm is estimated using Eq. (1) at $l_0 \leq 2$ nm. Based on this simple model, the relation between the growth rate of the nanorods $\dot{l}$ and the deposition rate $\dot{d}$ is written as $\dot{l}=\gamma l \dot{d}$. Since the nanowires will be covered by the growing grains for $\dot{l}<\dot{d}$, the geometrically determined condition of $\gamma l_0 > 1$ is applicable to the nanowire growth. In this study, no nanowires are observed for $\alpha=58°$, while nanowires with a length of more than 3 μm are formed when $\alpha=73°$ despite the fact that the difference in the value of $\tan\alpha$ is not very large. This strong dependence of the nanowire formation on the value of α can be attributed to the crossover of the magnitude relation between $\dot{l}$ and $\dot{d}$ as well as the α-dependent nucleation process for the nanowires.

Engineering of metal whiskers on the flat substrate by simple evaporation has never been reported because both the origin and key parameter of whisker nucleation were unknown. We infer that HT-GLAD is essential for the nucleation of nanorods and nanowires and it provides a method for the production of metal whiskers.

In summary, we investigated the morphology of the Al films deposited obliquely on the substrate maintained at 400 °C. The usual oblique columnar structures disappeared and the rough granular morphology was attributed to the enhancement of surface diffusion. In addition, two types of whiskers—nanorods and nanowires with diameters of approximately 560 and 50 nm, respectively—grew only on the sample prepared under the GLAD condition. In particular, GLAD was essential for the creation of whiskers during the initial stage of their growth. Since the growth mechanisms of whiskers of various metals are probably the same as those of Al whiskers, HT-GLAD will be useful for the production of nanorods and nanowires.

This study was supported by the 21st Century COE Program "Center of Excellence for Research and Education on Complex Functional Mechanical Systems."

[1] W. K. Burton, N. Cabrera, and F. C. Frank, Philos. Trans. R. Soc. London, Ser. A **243**, 299 (1951).
[2] T. Motohiro and Y. Taga, Appl. Opt. **28**, 2466 (1989).
[3] K. Robbie, M. J. Brett, and A. Lakhtakia, J. Vac. Sci. Technol. A **13**, 2991 (1995).
[4] K. Robbie, M. J. Brett, and A. Lakhtakia, Nature (London) **384**, 616 (1996).
[5] R. Messier, T. Gehrke, C. Frankel, V. C. Venugopal, W. Otaño, and A. Lakhtakia, J. Vac. Sci. Technol. A **15**, 2148 (1997).
[6] M. Suzuki and Y. Taga, Jpn. J. Appl. Phys., Part 2 **40**, L358 (2001).
[7] T. Karabacak, A. Mallikarjunan, J. Singh, D. Ye, G. Wang, and T. Lu, Appl. Phys. Lett. **83**, 3096 (2003).
[8] C. M. Zhou and D. Gall, Appl. Phys. Lett. **88**, 203117 (2006).
[9] J. Wang, H. Huang, S. V. Kesapragada, and D. Gall, Nano Lett. **5**, 2505 (2005).
[10] A. J. Melmed and R. Gomer, J. Chem. Phys. **34**, 1802 (1961).
[11] D. J. Barber, Nature (London) **194**, 272 (1962).
[12] I. A. Blech and E. S. Meieran, J. Appl. Phys. **40**, 485 (1969).
[13] M. Saka and R. Ueda, J. Mater. Res. **20**, 2712 (2005).
[14] I. A. Blech, P. M. Petroff, K. L. Tai, and V. Kumar, J. Cryst. Growth **32**, 161 (1975).
[15] K. Hinode, Y. Homma, and Y. Sasaki, J. Vac. Sci. Technol. A **14**, 2570 (1996).
[16] G. W. Sears, Acta Metall. **3**, 361 (1955).