Preferentially Oriented Growth of Aluminum under High Rate Deposition on Cleaved NaCl Crystals

Shigeo Sugawara and Shunji Ishio

Department of Materials Engineering and Applied Chemistry, Mining College, Akita University, Tegata, Akita 010, Japan

Simultaneous evaporation of Al (99.999% in purity) from dual sources of W baskets was carried out onto a surface of NaCl crystal cleaved in an ordinary high vacuum (10^{-3} Pa), and the crystallinity of the deposited film was examined through a transmission electron microscope (TEM). The substrate temperature varied in the range from room temperature to 523 K during the preparation of Al films of thickness 100 nm. On the other hand, the deposition thickness was changed from 20 to 130 nm at a substrate temperature of 473 K. A continuous single-crystal film with the (111) plane of thickness more than 70 nm was obtained on a substrate heated to 473 K.

(Received March 23, 1995)

Keywords: aluminum, thin film, vacuum deposition, epitaxial growth, sodium chloride, transmission electron microscopy

I. Introduction

Thin single-crystal films of metallic materials are often required for utilization as samples for physical experiments in various research fields. One of the most convenient ways to obtain such films is to deposit the materials on alkali halide crystals cleaved in air or in vacuum at an elevated substrate temperature. In many cases, however, deposited films are discontinuous and/or contain numerous grains showing some types of crystallographic orientation. On the contrary, some films of such materials as $\text{Ag}^{(1)(2)}$, $\text{Cu}^{(2)(3)}$, $\text{Au}^{(2)(4)(5)}$, which are obtained under specific evaporation conditions, are continuous and show only a few grains with different orientations.

As for Al films, many efforts have also been made to prepare single-crystal ones by vacuum deposition. Ino *et al.*⁽³⁾ obtained epitaxial films having two types of variants with the crystallographic orientation relationship of $(001)_{\text{NaCl}} // (111)_{\text{Al}}$, $[110]_{\text{NaCl}} // [\bar{1}\bar{1}0]_{\text{Al}}$ or $[\bar{1}\bar{1}0]_{\text{NaCl}} // [110]_{\text{Al}}$, when they deposited Al films from a W filament onto a NaCl crystal which was heated to temperatures above 373 K and then cleaved in an ordinary high vacuum (10^{-2} – 10^{-3} Pa) and an ultrahigh vacuum (10^{-5} – 10^{-7} Pa): the thickness of deposited films was 40–50 nm, the rate of film growth was lower than 1 nm/s and the domain size in films was estimated to be larger than a few microns. On the other hand, Dumpich and Wassermann⁽⁶⁾ employed a thick W filament of 7 mm in diameter for high-rate evaporation onto air-cleaved and heated NaCl substrates, and they reported that the discontinuity of Al films with a (111) preferred orientation was improved when evaporation rates increased from 27 to 33 nm/s, substrate temperatures higher than 603 K and system pressures lower than 7×10^{-5} Pa. In the same way, Al films were evaporated onto heated and cleaved KCl crystals in ultrahigh and ordinary vacuums⁽⁵⁾, which was

found to favor a (100) orientation of deposited films with increasing the substrate temperature above 473 K. Al films were also deposited on KBr substrates heated and cleaved in an ordinary high vacuum⁽⁷⁾, however, the deposited films showed a (111) textured structure. Another technique, which may improve the epitaxial growth of some metals, is the deposition of a thin layer of LiF on air-cleaved and heated NaCl prior to the metal deposition⁽⁸⁾, but the crystallinity of Al films thus obtained was not described in the literature.

From these results, it is inferred that vacuum cleavage⁽³⁾ has effects of lowering a critical epitaxial temperature and expanding a domain size largely, and that a high evaporation rate⁽⁶⁾ is advantageous in preparing an epitaxial Al film with improved continuity. Thus we have been interested in an effect of a combination of vacuum cleavage and high-rate evaporation. In vacuum deposition from a W filament, there are several ways to get a high evaporation rate. First, we can reduce a distance between an evaporation source and a substrate for this purpose. However, it is inadequate to reduce it to less than 5 cm, because radiant heat from the filament will have a marked thermal effect on the substrate. Next, increasing a current for the filament is another simple way to increase an evaporation rate. In fact, once Al melts during evaporation, a current can pass through molten Al, which covers a surface of a W wire, more easily than through the W wire with a higher electrical resistivity. Under such a condition, the increase of the current does not serve efficiently as a heat source for evaporation. Finally, we have found that adoption of two baskets is quite effective to get a high evaporation rate of Al. The present study shows that the deposition of Al from dual sources of W baskets onto a NaCl substrate preheated and cleaved in an ordinary high vacuum can lead to the growth of continuous (111) single-crystal films.

II. Experimental Procedure

Figure 1 shows the arrangement of two conical W baskets for evaporating Al (99.999% in purity) and a stage for heating and cleaving a NaCl substrate (parallelepiped $1 \times 5 \times 5 \text{ mm}^3$) in vacuum in a belljar. The two neighboring baskets made of a W wire 0.5 mm in diameter are separated by about 2 cm and aligned parallel to a $\langle 100 \rangle$ direction of the NaCl crystal. In addition the baskets are placed above the substrate at a distance of about 5 cm. Except for deposition onto the substrate at room temperature, Al in the dual baskets was evaporated after the substrate temperature reached an elevated point, and then the NaCl substrate was cleaved by pushing with a rod. The degree of vacuum was about 3×10^{-3} Pa before evaporation. In order to clarify the effect of substrate temperature on the epitaxy of Al, the substrate temperature varied from room temperature to 523 K for preparation of Al films 100 nm thick. Moreover, the deposition thickness varied from 20 to 130 nm for a substrate temperature of 473 K to reveal the change of the crystallinity of deposited films with increasing the thickness. The rate of film growth was 2–6 nm/s. In addition, evaporation of Al from a single source of W basket was carried out for comparison of the deposition on NaCl preheated at 473 K and cleaved in an ordinary high vacuum.

After successive evaporation of C was carried out onto the deposited Al film for reinforcement, the film was stripped from the substrate by immersion into distilled water and was mounted on Cu grids for the examination with a TEM (JEOL, JEM-200A). Then TEM observations were made under an accelerating voltage of 100 kV and a selected area diffraction pattern (SADP) was taken to examine crystallinity of the film obtained.

Fig. 1 Arrangement of dual W baskets and a stage for heating and cleaving a NaCl crystal in vacuum.

III. Results and Discussion

1. Effect of substrate temperature on the epitaxy

Electron micrographs and SADP's which were taken from the Al deposited films are shown in Fig. 2. When Al in the dual baskets was evaporated simultaneously on a NaCl substrate, cleaved in an ordinary high vacuum at room temperature, numerous fine grains were found in the films of thickness 100 nm (Fig. 2(a)) and the SADP consisted of a series of continuous and concentric Debye-Scherrer rings (Fig. 2(b)): the rings observed from the most inner part to the outer ones were ascribed to low-indexed reflections, respectively. This indicates that no epitaxial growth occurred on the substrate at room temperature.

On the other hand, a film deposited at a substrate temperature of 423 K (Fig. 2(c)) consisted mainly of continuous texture with a (111) preferred orientation as we can see from the corresponding SADP showing a relatively strong reflection and other weak ones (Fig. 2(d)). Moreover, evaporation of Al on the substrate at a temperature of 473 K led to epitaxial growth of a continuous (111) single-crystal film (Figs. 2(e) and (f)), although some small grains were still visible as dark spots in Fig. 2(e). The area of a single crystal ranged over a larger part than 10^3 – $10^4 \mu\text{m}^2$. In the same figure we can see some fine lines running parallel with each other from a lower left part to an upper right one. It seems that the lines were originated from surface steps produced on the substrate during cleavage. However, with increasing substrate temperature to 523 K considerably large domains developed to show two types of variants with a crystallographic orientation relationship of $(001)_{\text{NaCl}} \parallel (111)_{\text{Al}}$, $[110]_{\text{NaCl}} \parallel [1\bar{1}0]_{\text{Al}}$ or $[1\bar{1}0]_{\text{NaCl}} \parallel [1\bar{1}0]_{\text{Al}}^{(3)}$ (Figs. 2(g) and (h)). The observed results support the following growth mechanism proposed by Ogawa *et al.*⁽⁵⁾. Raising the substrate temperature facilitates migration of evaporated atoms on a substrate surface so as to meet and combine with other atoms, resulting in the formation of nuclei with a (111) orientation: in this case the bond direction of a nucleus tends to become parallel to the nearest neighbor direction in the sublattice of either kind of ions of a NaCl substrate. However, when the substrate temperature is too high, high energy of thermal vibration disturbs the arrangement of Al atoms, and it brings about the production of nuclei with a different orientation.

According to the experiments carried out for comparison, evaporation of Al from a single basket onto a NaCl substrate heated and cleaved in vacuum resulted in a discontinuous film, which was composed of grains with two types of variants in the (111) epitaxy, as shown in Fig. 3. For the preparation of continuous single-crystal films it is necessary to evaporate Al in dual baskets onto a substrate of NaCl heated to an optimum temperature of 473 K and cleaved in an ordinary high vacuum.

After a series of experiments, an additional observation was carried out on such a film as shown in Fig. 2(e)

Fig. 2 Electron micrographs and diffraction patterns of Al films formed by evaporation from dual sources of W baskets onto NaCl crystals cleaved in an ordinary high vacuum. The film thickness was 100 nm. The substrate temperatures were room temperature ((a) and (b)), 423 K ((c) and (d)), 473 K ((e) and (f)) and 523 K ((g) and (h)).

Fig. 3 Electron micrograph (a) and diffraction pattern (b) of an Al film formed by evaporation from a single source of W basket onto a NaCl crystal cleaved in an ordinary high vacuum. The film thickness was 100 nm and the substrate temperature was 473 K.

Fig. 4 Electron micrographs and diffraction patterns of Al films formed by evaporation from dual sources of W baskets onto NaCl crystals heated at 473 K and cleaved in an ordinary high vacuum. The film thicknesses were 20 nm ((a) and (b)), 50 nm ((c) and (d)) and 70 nm ((e) and (f)).

in order to examine thermal stability of small grains contained in a single-crystal film. As the film was heated up to about 873 K with the use of a heating device⁽⁹⁾ equipped in a TEM, the grains shrunk gradually and finally disappeared. Thus this suggests that heating at higher temperatures is more effective to get grain-free Al films. Further details will be reported in the near future.

2. Effect of deposited thickness on the epitaxy

A clue to make clear the process of epitaxial growth of Al during vacuum deposition would be provided by examining crystallinity of thinner films having different thicknesses prepared by the same preparation procedure as before except for keeping the substrate temperature at 473 K. Observed results are shown in Fig. 4. When the film thickness was 20 nm, the continuous film contained many small grains (Fig. 4(a)). They showed a (111) preferred orientation accompanied with some other ones such as a (100) orientation (Fig. 4(b)). At the film thickness of 50 nm the number of grains decreased considerably and each domain enlarged (Fig. 4(c)); two types of variants in the (111) epitaxy became outstanding in the texture (Fig. 4(d)). Single-crystal films with a (111) orientation developed at the thicknesses above 70 nm, as shown in Figs. 4(e) and (f). These facts suggest that misaligned grains would shrink or be rearranged as the film thickness increases, hence the film orientation can be greatly improved.

As pointed out in Section III.1 the Al films deposited from a single source were discontinuous (Fig. 3), while those deposited from dual sources were continuous although numerous grains with different orientation relationships were found in the early stage of deposition (Fig. 4(a)). From these results it is assumed that the vacuum deposition from a single source might result in the minor coarsening and rearrangement of nuclei formed in

the initial stage of film growth, whereas the faster coalescence of many nuclei produced during deposition from dual sources would lead to the preferred growth of film.

IV. Conclusion

We prepared thin films by evaporating Al from dual sources onto a NaCl crystal cleaved in an ordinary high vacuum. The (111) continuous single-crystal films of thickness 100 nm grew on the substrate, when heated up to 473 K. From the fact that many small grains were contained in the thin films of thickness 20 nm, we inferred that the fast coalescence and rearrangement of numerous nuclei formed in an early stage of vapor deposition might be essential for the growth of Al (111) single-crystal films.

Acknowledgment

We appreciate Mr. Y. Nomura for his help in the experiments.

REFERENCES

- (1) B. W. Sloope and C. O. Tiller: *J. Appl. Phys.*, **32** (1961), 1331.
- (2) S. Ino, D. Watanabe and S. Ogawa: *J. Phys. Soc. Jpn.*, **17** (1962), 1074.
- (3) S. Ino, D. Watanabe and S. Ogawa: *J. Phys. Soc. Jpn.*, **19** (1964), 881.
- (4) C. Sella and J. J. Trillat: *Single-Crystal Films*, ed. by M. H. Francombe and H. Sato, Pergamon Press, New York, (1964), p. 201.
- (5) S. Ogawa, S. Ino, T. Kato and H. Ota: *J. Phys. Soc. Jpn.*, **21** (1966), 1963.
- (6) G. Dumpich and E. F. Wassermann: *Surf. Sci.*, **33** (1972), 203.
- (7) T. Kato: *Jpn. J. Appl. Phys.*, **7** (1968), 1162.
- (8) S. Köster, N. Herres, M. Rey and K. Reichelt: *J. Appl. Phys.*, **59** (1986), 278.
- (9) J. Watanabé, S. Sugawara and A. Funato: *Trans. JIM*, **27** (1986), 939.