Title: Growth of Metal Nanowhiskers on Patterned Substrate by High Temperature Glancing Angle Deposition

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In this study, we carry out high temperature glancing angle deposition (HT-GLAD) of Fe and Al on a heated substrate with trench patterns. When vapor is incident perpendicular to the trench direction, nanowhiskers grow only on the surface exposed to the vapor and not inside the trenches. When vapor is incident at a deposition angle larger than 80° on the sidewall of the trench and not on the substrate surface, nanowhiskers grow only on the sidewall because the condition of deposition at a high temperature and a large deposition angle is satisfied only for the sidewall. Thus, we succeed in the selective growth of nanowhiskers by controlling the geometrical deposition conditions. Further, we also discuss the effect of the local deposition geometry on the growth process.

Geometrically selective growth by HT-GLAD is expected to be useful for growing nanowhiskers on nano- and microstructured substrates.

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Selective growth of nanowhiskers by shadowing effect.— During HT-GLAD, vapor flux is incident on the substrate at a large deposition angle; therefore, only the convex parts and not the concave parts of the surface are exposed to the vapor flux. Thus, if we use a prepatterned substrate, as is often the case in the selective growth of nanowhiskers, we can achieve a patterned growth of nanowhiskers.

In this study, to verify the selective growth of nanowhiskers by the shadowing effect, we carried out the HT-GLAD of Fe on a Si(001) substrate with periodic V-shaped grooves along the [110] direction. Fe vapor was incident at a deposition angle of 82° in such a way that the plane of incidence was perpendicular to the direction of the grooves; therefore, most parts of the grooves were shadowed from the Fe vapor. During deposition, the substrate temperature was maintained constant at 470°C, and the average thickness of deposited Fe was 48 nm.

Results and Discussion

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Figure 2 shows typical SEM images of the resultant samples. As expected, many Fe nanowhiskers with diameters of 50–200 nm and lengths up to 500 nm grew only on the ridges of the pattern. No significant deposition occurred on the shadowed parts of the grooves. This indicates that the diffusion length of the adatoms is considerably shorter than the size of the grooves. For the nucleation of nanowhiskers to occur in HT-GLAD, long-distance diffusion of adatoms is not required. From the SEM images, the diffusion length of adatoms on the surface was estimated to be of the order of 100 nm. Therefore, it would be possible to achieve the selective growth of nanowhiskers by the shadowing effect on nanopatterns with a size down to a few hundred nanometers.

Selective growth of nanowhiskers by control of deposition angle.— Because the growth process of nanowhiskers by HT-GLAD is very sensitive to the deposition angle (reported by us in a previous study), in this study, the selective growth of Al nanowhiskers was carried out on sidewalls of rectangular trenches. Aluminum was deposited on a micropatterned Si[110] substrate with native oxide. Six groups of trenches with nominal widths of 1, 3, 5, 10, 15, and 20 μm and a depth of 1.7 μm were prepatterned along the [110] direction. During deposition, the substrate temperature was maintained constant at 390°C. By selecting appropriate polar and azimuth angles of the substrate during the deposition process, deposition angles on both the surface and the sidewalls of the trenches were controlled independently. Figure 3a shows schematic representations of the deposition geometry. The polar angle ϑ was defined as the angle between the substrate normal and the incident direction of the deposition flux, and the azimuth angle φ was defined as the angle between the trench direction and the plane of incidence of the Al vapor. As shown in Fig. 3b, the deposition angle on the surface was equal to α, whereas that on one of the sidewalls (illuminated sidewall) was γ = cos⁻¹(sin α sin φ). Samples were prepared at dif-
different values selected between 55 and 85°; however, γ was fixed at 85°. The average thickness of Al deposited on the illuminated sidewall was 23 or 30 nm.

Figure 4 shows typical SEM images of a cross section of samples prepared on trenches for [(a) and (b)] α = 55° and [(d) and (e)] 85°. Thin and long nanowhiskers grow on both types of the samples. Because nanowhiskers grow only under the condition of deposition at a high temperature and at a deposition angle larger than 80°,1 in α = 55°, they grow only on the sidewall and not on the surface or the bottom of the trenches. For α = 85°, many nanowhiskers grow on the surface, bottom, and sidewalls of the sample. Thus, the selective growth of nanowhiskers was successfully carried out by controlling the geometrical deposition conditions.

The growth of nanowhiskers on the sidewalls of the trench is not a simple phenomenon. In Fig. 4a and d, it can be observed that nanowhiskers grow not only on the illuminated sidewalls but also on the shadowed sidewalls that have never been directly exposed to the vapor flux. Surprisingly, the growth of nanowhiskers on the shadowed sidewalls is not exceptional, while the number of nanowhiskers grown on the shadowed part of the bottom is small. Figure 5 shows the SEM images captured from various angles for the same two samples: with α = 55° (Fig. 5a) and α = 85° (Fig. 5b-d). As observed in Fig. 5a and b, the nanowhiskers grow on the shadowed sidewalls of both the samples. Further, many islands or grains as well as nanowhiskers are present on the surface, part of the bottom exposed to the incident vapor, and on illuminated sidewalls. The morphological features observed in Fig. 5e are characteristic of the samples prepared by HT-GLAD, as reported in our previous papers.1,2 However, no recognizable islands or grains are present on the shadowed sidewalls, and only thin and long nanowhiskers grow.
on these sidewalls (Fig. 5d). Few nanowhiskers grow on the shadowed part of the bottom (Fig. 5b and d). This suggests that the re-evaporation or reflective scattering of atoms deposited on the sidewalls of the trenches contributes to the growth of nanowhiskers.

**Effects of local deposition geometry on growth of nanowhiskers.**— In addition to the growth of nanowhiskers on the shadowed sidewalls, note that the size and number of nanowhiskers growing on the sidewalls depend strongly on $\alpha$. Figure 6 shows a plan view of samples prepared at $\alpha = 73, 84,$ and $87^\circ$. As schematically indicated under each SEM image, the incident direction of Al vapor under the condition of large $\alpha$ is more parallel to the trenches than that under the condition of small $\alpha$. At $\alpha = 73^\circ$, only a few short nanowhiskers grow on the sidewalls, whereas at large $\alpha$, many long nanowhiskers grow on the sidewalls of the trenches. Figure 7 shows the relation between $\alpha$ and the number density of nanowhiskers grown on the sidewalls for the samples with an average Al thickness of 30 nm. Clearly, the number of nanowhiskers drastically increases for $\alpha \geq 80^\circ$.

Next, we discuss the effect of the deposition geometry on the growth of Al nanowhiskers. Because $\gamma$ is fixed to $85^\circ$ and the amount of Al deposited on the sidewall is constant at 30 nm, the number and size of the nanowhiskers should not change if deposition is carried out on a large flat substrate. Ordinary diffusion processes cannot satisfactorily explain this $\alpha$ dependence of the number of nanowhiskers. In the deposition on the sidewalls of the trenches, the distance from the trench edge to the growth point changes significantly with a change in $\alpha$. If atoms deposited in front of the growing nanowhiskers contribute to the growth by re-evaporation or scattering, the dependence of the number and size of nanowhiskers on $\alpha$ may be understood.

In fact, it has been reported that the sticking coefficient of metals on some oxide substrates is extremely small even at a few hundred degrees Celsius. For example, Benck et al.\textsuperscript{16} reported the sticking of Ag deposited on some oxides as a function of the substrate temperature. The significant amount of Ag was deposited at large deposition angles in their experimental setup. Remarkably, even at $300^\circ$C, the sticking coefficient of Ag on SiO$_2$ is smaller than 0.3. The sticking coefficient of Al on SiO$_2$ may be similar. If atoms reflected on the surface in front of the growing nanowhiskers also contribute to their growth, the growth rate increases significantly.

We used a conventional growth model\textsuperscript{1,11,17} to estimate the contribution of reflected atoms to the nanowhisker growth. Figure 8 shows the growth model of nanowhiskers on the sidewall of a trench. In this conventional growth model, adatoms diffuse over the sides of the nanowhiskers and are incorporated at the top of the nanowhiskers. As an extreme case of the fastest growth, we assume that all atoms impinging upon the nanowhiskers are incorporated into the nanowhiskers and that their radius does not change during the growth process. Evaporated atoms are directly incident on the side of a nanowhisker of length $l$ growing at a distance $w$ from the edge of the substrate. Here, the vapor flux incident on the surface of the side of the nanowhisker is $f \tan \gamma$, where $f$ is the component of the vapor flux perpendicular to the surface. We assume that the atoms reflected on the surface in front of the nanowhisker also contribute to the nanowhisker growth. Here, we also assume that the reflectance of the atoms is $s$. The length of the nanowhisker depending on the reflectivity of the atoms is written as

**Figure 6.** (Color online) SEM images of plan view of samples with (a) $\alpha = 73^\circ$, (b) $\alpha = 84^\circ$, and (c) $\alpha = 87^\circ$. The average thickness of deposited Al is 30 nm; further, $\gamma = 85^\circ$ for all samples. The deposition geometries are indicated schematically under each SEM image.

**Figure 7.** Relation between $\alpha$ and number density of nanowhiskers growing on sidewalls for samples with average Al thickness of 30 nm.

**Figure 8.** Growth model of nanowhiskers on sidewalk of trench.
not all adatoms might be incorporated into the nanowhiskers, and rough surfaces. In our previous paper, we reported that there are a result is consistent with the experimental results shown in Fig. 7. whiskers grow, it may be easy to find many nanowhiskers. This whiskers depends on $s$ from a small nucleus. Further, in this case, the length of the nano- = 0 is small. For nanowhiskers growing on the sidewall at a depth $l_0 = 0.1$ nm. In addition to assuming the height of nuclei, we assumed typically used values or typically observed values in the experiments ($d = 30$ nm, $r = 30$ nm, $w_0 = 50$ nm, and $\gamma = 85^\circ$). For $s = 0$, i.e., in the case that the reflected atoms do not contribute to the nanowhisker growth, the length of the nanowhiskers is independent of $\alpha$. The length of nanowhiskers grown at $s = 0$ is small. For $s \neq 0$, i.e., in the case that the reflected atoms contribute to the nanowhisker growth, long nanowhiskers can grow from a small nucleus. Further, in this case, the length of the nanowhiskers depends on $\alpha$. Under the condition where the long nanowhiskers grow, it may be easy to find many nanowhiskers. This result is consistent with the experimental results shown in Fig. 7.

The above-mentioned model is also useful in understanding the growth mechanism of very long nanowhiskers on substrates with rough surfaces. In our previous paper, we reported that there are a significant number of nanowhiskers with lengths considerably greater than that predicted by the conventional model ($s = 0$ in Eq. 1) and that the number of long nanowhiskers is independent of the surface roughness under the same deposition condition with this study except for the substrate. In fact, if $s = 0$, from Eq. 1, the length $l_0$ of the nucleus should be approximately 250 nm for the growth of the typical long nanowhisker reported in Ref. 13 having $l_0 = 7$ $\mu$m and $2\sigma = 100$ nm at $d = 23$ nm and $\gamma = 85^\circ$. In practice, not all adatoms might be incorporated into the nanowhiskers, and the diameter of the nanowhiskers could increase; therefore, the growth rate of nanowhiskers should be smaller than that predicted by Eq. 1. Clearly, results yielded by the conventional model are inconsistent with the observation of the growth of long nanowhiskers in our study. It is strongly suggested that a significant amount of AI is supplied to the nanowhiskers both via direct deposition on their side surface and from the surrounding region. However, ordinary surface diffusion cannot explain the fact that long nanowhiskers can grow on a very rough surface. If we take into account the contribution of atoms reflected on the surface in front of nanowhiskers to nanowhisker growth, long nanowhiskers can easily grow from small nuclei. The growth of nanowhiskers on the shadowed sidewall may be attributed to the contribution of reflected or scattered atoms. Therefore, we can say that atoms reflected or scattered on the surface in front of nanowhiskers significantly contribute to the growth of long nanowhiskers by HT-GLAD.

Conclusions

We carried out the HT-GLAD of Fe and Al on a heated substrate with trench patterns. Nanowhiskers selectively grew on the substrate by the shadowing effect and under controlled geometrical deposition conditions. In the growth of Al nanowhiskers on the sidewalls of the trenches, nanowhiskers grew not only on illuminated sidewalls but also on shadowed sidewalls. In addition, the size and number of nanowhiskers growing on the sidewalls depended strongly on $\alpha$, although $\gamma$ was maintained constant. The reflective scattering of atoms on the surface in front of nanowhiskers plays an important role in the growth of nanowhiskers.

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