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Title	Characterization of α-phase aluminum oxide films deposited by filtered vacuum arc
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Citation	Surface and Coatings Technology, 142-144: 260-264
Issue Date	2001-07
Type	Journal Article
Text version	author
URL	http://hdl.handle.net/10119/4967
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Description	

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Published in Surface and Coatings Technology 142-144 (2001) pp.260-264.

Characterization of α-phase aluminum oxide films deposited by filtered vacuum arc

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Abstract

Aluminum oxide (Al_2O_3) films were deposited by filtered vacuum arc method, using highly pure aluminum cathode and oxygen gas. Substrate temperature as high as 780 ˚C was necessary for the formation of corundum structured α-Al_2O_3. Applying RF power and thus negative bias voltage to the substrate enables to increase and control the energy of substrate bombarding ions. With the negative bias voltage of 200V, it was possible to deposit films containing α-Al_2O_3 with preheating substrate to temperature lower than 500˚C. Increasing the voltage, thus increasing the ion energy, resulted in lowering of the critical preheating substrate temperature for formation of α-phase. Additionally, there was a clear difference in crystal orientation of α-Al_2O_3 between the films grown with and without substrate bias voltage, which was confirmed by infrared spectroscopy. Structure and phase evolution of the film were also studied by cross-sectional transmission electron microscopy.

Keywords: B. Infrared spectroscopy ; B. RBS ; B. TEM ; C. Filtered arc; C. Ion bombardment ; D. Aluminum oxide

1. Introduction

Deposition of aluminum oxide film from vapor phase is of great interest in many fields, such as wear resistant coatings for cutting tools, insulating layer for the semiconductor devices, oxygen permeation barrier coatings for the turbine blades, or hydrogen permeation barrier coating for the nuclear fusion reactors.

The only thermodynamically stable phase of Al_2O_3 is corundum structured α-phase. Besides this phase, Al_2O_3 has a number of metastable polymorphs, such as γ-phase, κ-phase, θ-phase etc. There are many methods to produce Al_2O_3 coatings from vapor phase. Chemical vapor deposition (CVD) methods use various aluminum containing gases and oxygen gas, and physical vapor deposition (PVD) methods use sputtered or evaporated solid aluminum (or alumina) and additional oxygen gas or ions. Macro- and micro-scopic structures of the deposited films depend highly on deposition processes and parameters. General tendency is that the phase formed in the deposited film depends strongly on substrate temperature. At low temperature region amorphous Al_2O_3 is dominant, at middle temperature region crystalline γ-phase becomes dominant, and at high temperature region crystalline κ-phase and α-phase become dominant. Dense and hard phases like κ-phase and α-phase, which is interesting for hard/wear-resistant coatings, require very high substrate temperature (over 1000˚C) in CVD methods. In PVD methods, such as reactive sputtering, reactive evaporation, ion plating, and cathodic arc, the temperature required for the dense phase is somewhat lower, around 700-800˚C, which is attributable to high kinetic energy of the depositing species. And by increasing the kinetic energy and controlling flux of the depositing species, it is possible to lower the substrate temperature even more. Zywitzki *et al* [1] reported that in reactive evaporation of aluminum with oxygen gas, it was possible to deposit Al_2O_3 film containing α-phase with plasma activation at substrate temperature of 700˚C, at which without plasma activation, α-phase did not form. Schneider *et al* [2] reported that in ionized magnetron

sputter deposition, it was possible to deposit κ-phase and θ-phase at substrate temperatures of 340-430˚C, which requires 1000˚C in CVD method.

In this paper, we report on the formation of α-phase in the Al_2O_3 films deposited by filtered vacuum arc method with additional RF bias voltage to the substrate. α-Al_2O_3 formed at substrate temperature as low as 460˚C owing to the ion bombardment during the film deposition. The layered structure of the film and the effect of the energetic ions to the crystal orientation were also studied, which provide an interesting insight to the understanding of ion-assisted formation and growth of dense phases.

2. Experimental

The aluminum oxide films were deposited on vanadium foils (0.25mm thick), silicon wafers, and a graphite disc, using the filtered vacuum arc method[3]. A schematic diagram of the apparatus is shown in Figure 1. The cathode material was 99.999% pure aluminum. The arc current was approximately 102.5A. The base pressure was less than 3×10^{-3}Pa. During the deposition, oxygen gas was added from the capillary near the substrate to pressure of 5.4 $\times10^{-2}$Pa. Substrates were preheated to temperatures ranging from room temperature to 800˚C by pyrolytic graphite heater covered with pyrolytic BN in substrate holder. Temperature rise during the deposition was not measured in this study, which means that substrate temperature is the temperature the substrate was preheated. In some deposition, RF bias voltage was applied to the substrate for the acceleration of the ionic species. Deposition rate without substrate bias voltage was about 2nm/s, depending slightly on the substrate temperature. Film thickness ranged from a few hundred nm to a few μm, which was controlled by deposition time. All the samples showed good adhesion without any visible cracks or delaminations.

The chemical composition of the film deposited on a polished graphite disc was characterized by Rutherford backscattering spectroscopy (RBS). ^{4}He ion beam accelerated to 1.5 MeV was used for the measurement. The sample was fixed so that the ion beam is normal to the substrate surface, and a detector was placed at 165° scattering angle. Total dose was 116μC. For calculating RBS spectra, SIMNRA 4.51 [4] was used.

The vibrational properties were studied by Fourier transform infrared reflection absorption spectroscopy (IRAS). IRAS measurements were done using bare vanadium foil as a background spectra specimen. Reflection mirrors were aligned so that the incident IR beam was 20° off normal.

The structures of the film were studied by cross-sectional transmission electron microscopy (TEM). For cross-sectional TEM observation, a specimen was prepared by focused ion-beam (FIB) etching apparatus with Ga ion beam. Before FIB etching, specimens were sliced and mechanically polished by SiC and diamond powder until the thickness was reasonably small.

3. Results

The result of RBS measurement of aluminum oxide film deposited on graphite disc together with the simulated spectrum (Al:O =0.394:0.606, thickness 8.75×10^{17} atoms/cm^2) is shown in Figure 2 (a). The film consisted of aluminum and oxygen in stoichiometric composition without any trace of metallic impurities. Slight amount of carbon was detected on sample surface, which is considered to be contamination from air. Combined with the film thickness (approx. 132nm) estimated from the deposition rate of the thicker film, density of the film was evaluated to be 2.2g/cm^3, which is 56% of the density of the bulk sapphire. Another Al_2O_3 film, which was deposited on vanadium foil with same condition, but with deposition time 10 times longer, was analysed with IRAS. The spectrum is shown in Figure 2 (b). It shows an absorption peak at 957cm^{-1} and a broad absorption peak around 630cm^{-1}.

These peaks can be assigned to the longitudinal optical (LO) mode and the transverse optical (TO) mode of amorphous Al_2O_3[5][6], respectively. The evaluated density and the phonon modes also suggest that this Al_2O_3 film is amorphous.

Figure 3 (a) shows IR spectra of films deposited for 10 minutes with different substrate temperatures. The films deposited below 690˚C exhibit IR spectra similar to the IR spectrum of amorphous Al_2O_3. An IR spectrum of the film deposited at 780˚C shows completely different absorption peaks. Three peaks at 427, 550, and 630cm^{-1} can be assigned to sapphire (α-Al_2O_3) TO modes with its c-axis normal to the electric field vector of the IR beam (E) (442, 569, and 635cm^{-1}, error 1%) [7]. Although observed peaks show shift from the assigned value, it is due to the large thickness, thus large absorption, of the film. A film with half thickness deposited with the same condition showed peaks at 437, 564, and 634cm^{-1}. X-ray diffraction analysis also confirms that the film contains α-Al_2O_3. A peak at the higher wavenumbers, around 932 cm^{-1}, should be LO mode peak. This peak is somewhat broad and is considered to be the combination of LO mode peaks (amorphous 959cm^{-1}[8]; γ-Al_2O_3 917cm^{-1}[8]; α-Al_2O_3, c-axis normal to E, 900cm^{-1}[7]; α-Al_2O_3, c-axis parallel to E, 871cm^{-1}[7]) of the phases existing in the film. These results indicate that the film deposited at 780˚C consists of α-phase and some other phase, and c-axis of the α-Al_2O_3 is normal, thus the basal plane of α-Al_2O_3 is parallel, to the substrate surface.

Figure 3 (b) shows IR spectra of films deposited with negative substrate bias voltage of 200V. At lower substrate temperature, the IR spectra show γ-Al_2O_3 like TO mode peaks[8]. Above 490˚C, the spectra are completely different. Two peaks at lower wavenumbers (578cm^{-1}, and weak absorption peak at 652cm^{-1}) can be assigned to TO modes of sapphire (α-Al_2O_3) with its c-axis parallel to E (583 and 654cm^{-1}, error 1%)[7]. LO mode peak (927cm^{-1}) seems like a mixed peak. The result indicates that in these films, c-axis of the α-Al_2O_3 is parallel, thus the basal plane of α-Al_2O_3 is normal, to the substrate surface.

Figure 4 is a cross-sectional TEM image of a film deposited on vanadium foil at substrate temperature of 580˚C with 200V negative bias voltage. Wedge shaped crystallites in upper part of the film, which is similar to the image in Ref.9, is apparent. Selected area diffraction confirmed that the layer near the substrate consists of amorphous and γ-Al_2O_3 with small crystal size, and that the wedge shaped crystallites are crystalline α-Al_2O_3. Coexistence of several phases supports the broad LO mode peaks in IR spectra.

Figure 5 shows an IR spectrum of an Al_2O_3 film deposited with 300V negative bias voltage. Substrate temperature was 460˚C, which failed to form α-Al_2O_3 with 200V negative bias voltage. The IR spectrum of α-Al_2O_3 containing film already shown in Fig. 3 (b) is also shown in the figure for comparison. Position of TO mode peaks of the new spectrum indicates that the film also consists of α-Al_2O_3 with its c-axis parallel to the substrate surface. Decrease in full width half maximum of the peak indicates the better crystallinity of the film. LO mode peak shows absorption at similar wavenumbers (926cm^{-1}), but the width of the peak of the spectrum of 300V sample compared to the spectrum from of 200V sample is smaller. This result indicates less amount of non-α-phase Al_2O_3, when deposited with ions with higher energy.

4. Discussions

The film structure observed in cross-sectional TEM image in this study was similar to the image observed by Zywitzki *et al.*[9] for the Al_2O_3 film deposited on stainless steel substrate with 760-770˚C substrate temperature and 50V substrate bias voltage using pulsed magnetron sputtering. Both images show the nucleation and subsequent growth of α-Al_2O_3 on γ-Al_2O_3, resulting in wedge shaped crystallites of α-Al_2O_3. Difference between the images is that for the film in this study, even with film thickness around 0.9μm, film surface

was mostly α-Al_2O_3, while the film in Ref.9 required at least 3μm to achieve the same state. This means that the film in this study had higher α-Al_2O_3 nucleation density and/or faster lateral growth speed compared to the film in Ref.9. According to our result of the depositions with different bias voltages, increase in bias voltage resulted in decrease of non-α-Al_2O_3. The voltage used in the work of Zywitzki *et al.* was smalll compared to this study, and this might be the main reason for the difference in structure observed in the TEM image.

The other interesting point is the crystallographic relationship of α-Al_2O_3 and substrate surface. In Ref.9, the crystallographic feature for the bias voltage applied sample was (100) and sometimes (210) lattice planes parallel to the substrate surface. This is consistent with the crystallographic relationship observed in this study for the bias applied samples. Therefore, it is possible to suggest from these results that the Al_2O_3 films deposited with different methods had similar structure, and that there is a common growth process for ion-assisted deposition of the Al_2O_3 film.

Ion bombardment during film deposition resulting in formation of dense phase is frequently observed, for example, *c*BN films[10] and diamond-like-carbon films[11]. In case of *c*BN films, there are some features which are common to α-Al_2O_3 film growth, such as, the layered structure[12] resulting from the dense phase nucleation and subsequent growth on initial layer, and the preferential orientation with one kind of axis lying in the plane parallel to the substrate surface[13]. These common features are a key to understand the growth mechanism of the films in ion-assisted methods.

5. Conclusion

Applying substrate bias voltage dramatically decreased the substrate temperature required for the formation of α-Al_2O_3. This is particularly important when coating materials like vanadium, which at high temperature oxidation proceeds faster. The effect of bias voltage on

crystal orientation and initial layer thickness of Al_2O_3 film is also interesting in aspect of ion assisted growth of dense phases. The evolution of the film, starting from amorphous Al_2O_3 and nanocrystalline γ-Al_2O_3 followed by nucleation and subsequent growth of α-Al_2O_3 resembles ion-assisted growth process of other materials, such as *c*BN. It would be useful to compare the growth processes of these materials for the better understanding of ion-assisted nucleation and growth mechanism.

Acknowledgment

The authors are grateful to T. Höschen for his contribution in deposition experiments, and to J. Perchermeier of IPP for his instruction and cooperation on use of FTIR spectrometer. The authors would also like to thank H. Sawada of the University of Tokyo for the TEM observation.

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Figure 1 Schematic diagram and deposition conditions of filtered vacuum arc apparatus.

Figure 2 (a) Measured and simulated RBS spectra of the aluminum oxide film deposited on a graphite substrate. Film thickness is around 130 nm. (b) Infrared spectra of the aluminum oxide film deposited on a vanadium foil substrate. Film thickness is around 1.2 μm.

Figure 3 Infrared spectra of the Al_2O_3 films deposited on vanadium foils by different substrate temperatures. (a) without bias voltage, (b) with negative bias voltage of 200 V.

Figure 4 Cross-sectional bright field TEM image of the film deposited on vanadium at 580˚C with 200V negative substrate bias voltage.

Figure 5 Comparison of infrared spectra of α-phase containing Al_2O_3 films deposited with different negative bias voltages.

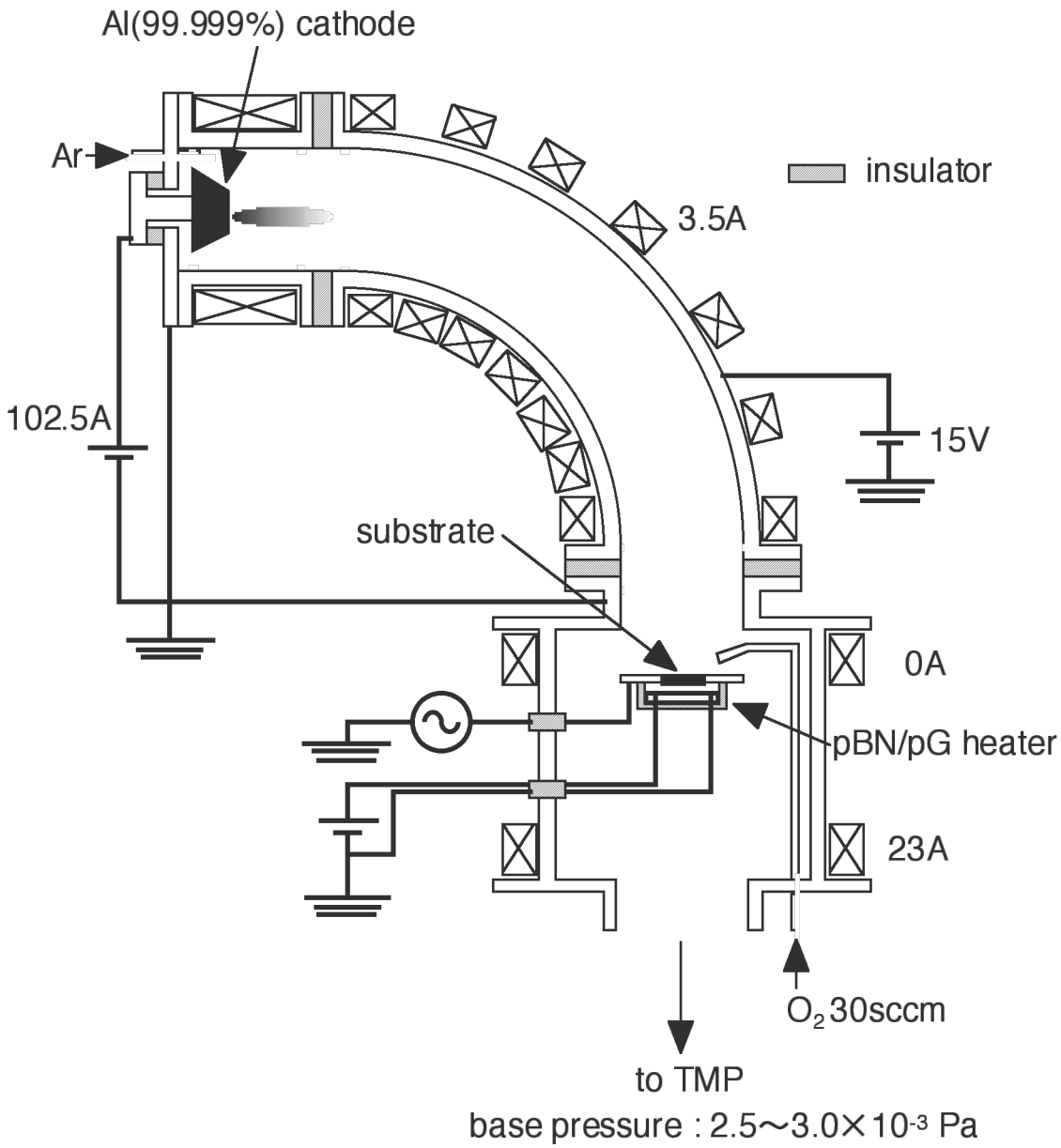
Al(99.999%) cathode
Ar
insulator
3.5A
102.5A
15V
substrate
0A
pBN/pG heater
23A
O_2 30sccm
to TMP
base pressure : 2.5~3.0×10^{-3} Pa

Fig. 1

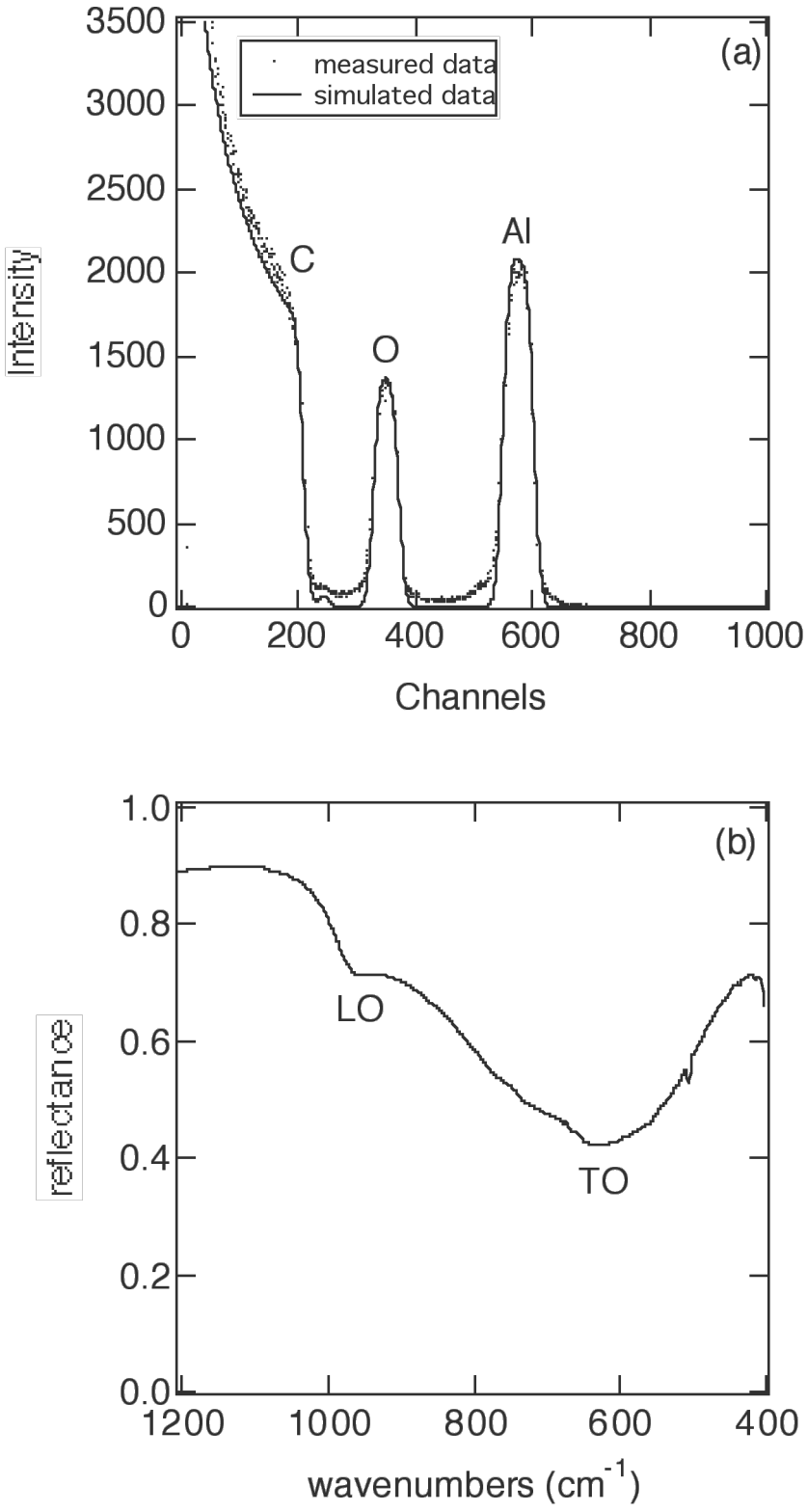
(a)
measured data
simulated data
C
O
Al
Intensity
Channels
(b)
LO
TO
reflectance
wavenumbers (cm-1)

Fig. 2

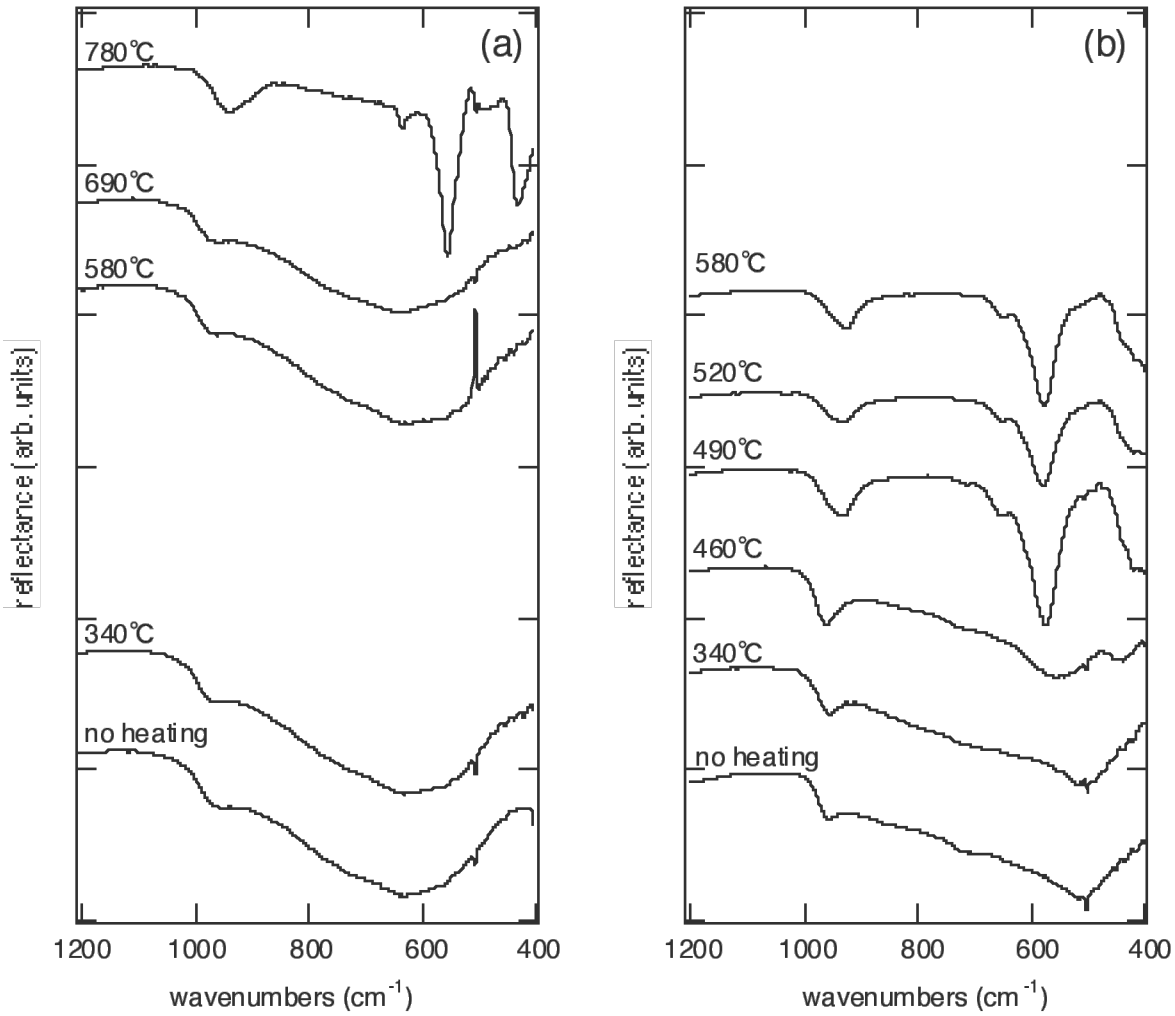
(a)
780℃
690℃
580℃
340℃
no heating
reflectance (arb. units)
1200
1000
800
600
400
wavenumbers (cm-1)
(b)
580℃
520℃
490℃
460℃
340℃
no heating
reflectance (arb. units)
1200
1000
800
600
400
wavenumbers (cm-1)

Fig. 3

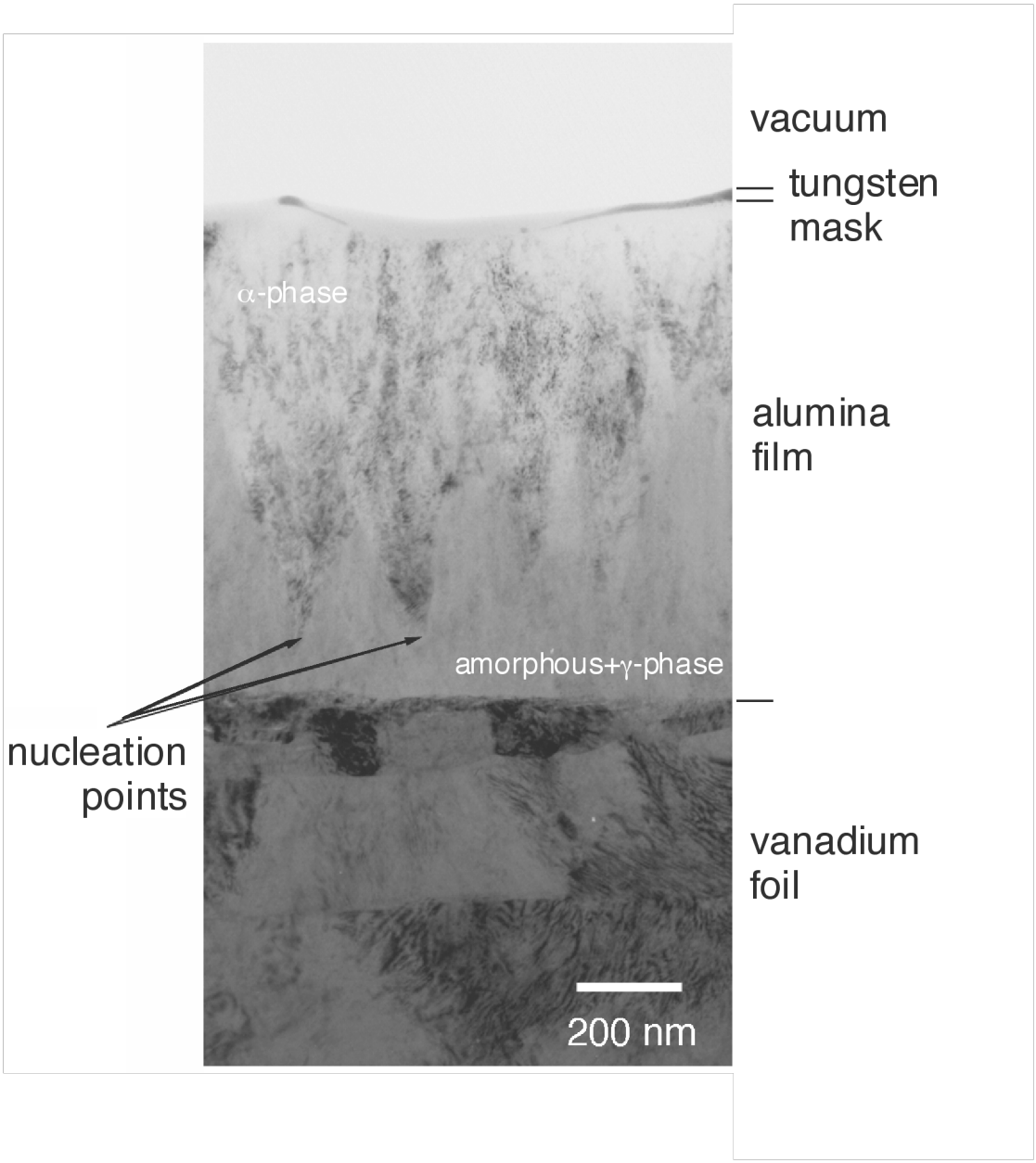
vacuum
tungsten mask
α-phase
alumina film
amorphous+γ-phase
nucleation points
vanadium foil
200 nm

Fig. 4

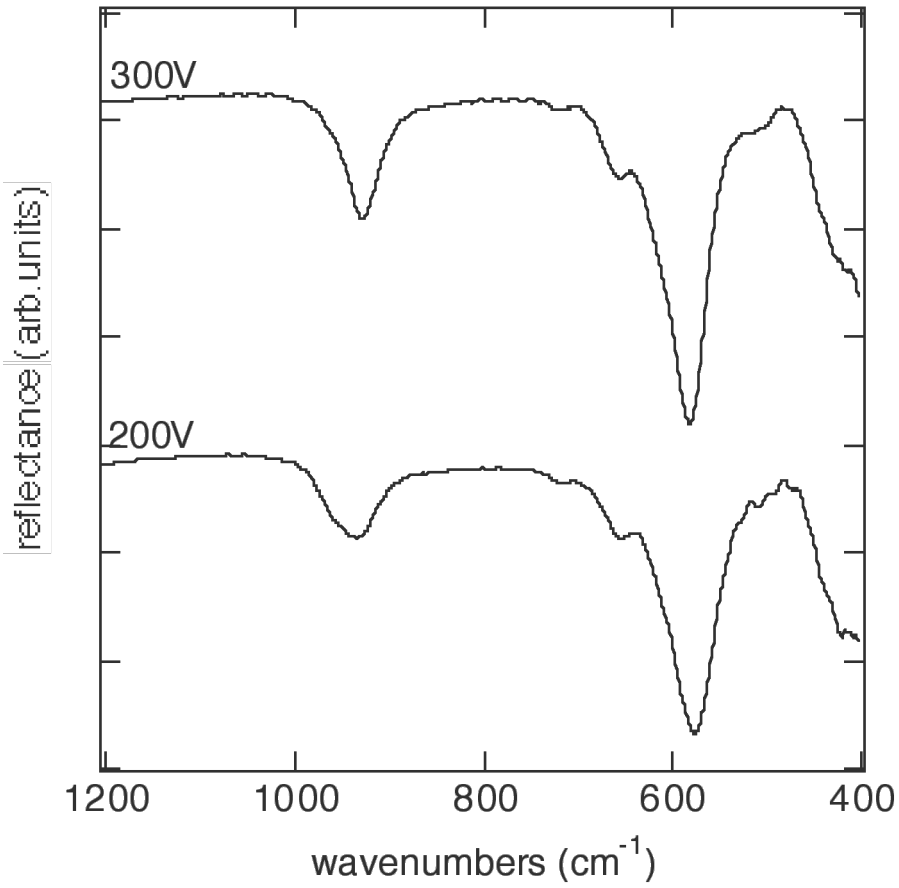
300V
200V
reflectance (arb.units)
1200
1000
800
600
400
wavenumbers (cm-1)

Fig. 5

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