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Inhibition of Field Crystallization of Anodic Niobium Oxide by Incorporation of Silicon Species

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Abstract

The present work demonstrates effective inhibition of field crystallization of amorphous anodic niobium oxide by incorporation of silicon species from substrate. The field crystallization, detrimental for capacitor application of niobium, occurs during anodizing of magnetron sputtered niobium at 100 V in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 333 K, while amorphous structure of the anodic oxide is totally retained during anodizing of magnetron sputtered Nb-12 at% Si. Even after prior thermal treatment in air, which accelerates field crystallization of anodic oxide on niobium, no crystallization occurs on the Nb-12 at% Si. Through examination of the crystallization behaviours of anodic films formed on a thin Nb-12 at% Si layer superimposed on a niobium layer as well as on a thin niobium layer superimposed on an Nb-12 at% Si layer, it has been confirmed that air-formed oxide or thermal oxide becomes a nucleation site for crystallization. Modification of the air-formed or thermal oxide by incorporation of silicon species inhibits the nucleation of crystalline oxide. The modification, however, does not influence the growth of crystalline oxide. The growth is suppressed by continuous incorporation of silicon species into anodic film from the substrate during anodizing.

Keywords: anodic oxide, niobium, field crystallization, dielectric oxide, silicon incorporation

1. Introduction

Tantalum electrolytic capacitors are currently used widely in various electronic equipments. However, limitation of natural resources of tantalum stimulates the development of alternative capacitor materials. Niobium is one of the promising alternative materials for tantalum electrolytic capacitors. The physical and chemical properties of these metals as well as their oxides are similar, but several drawbacks, including high leakage current, bias potential dependence of the capacitance, and high susceptibility for crystallization of oxide, have been pointed out for niobium capacitors [1]. In tantalum and niobium electrolytic capacitors, dielectric layers are developed by anodizing of these metals. The anodic oxides formed on niobium and tantalum are usually amorphous, but during anodizing at relatively high voltages and at increased temperatures of electrolyte, crystalline oxide is nucleated in growing amorphous anodic oxide under the high electric field [2-6]. Such crystallization is referred to as field crystallization [3], and niobium is more susceptible for the field crystallization than tantalum [6]. Since the field crystallization causes degradation of the dielectric properties [7], this must be inhibited during formation of dielectric niobium oxide for fabrication of high performance niobium capacitors.

Once crystalline oxide is nucleated in growing amorphous anodic oxide during anodizing of niobium and tantalum, thickening of the crystalline oxide region is more rapid than that of the surrounding amorphous oxide region during anodizing at constant formation voltage, causing cracking and subsequent turning up of the outer amorphous oxide layer [5, 8]. It has been reported in the 1950s that inclusions in metal substrates act as an initiation site of field crystallization when they are incorporated from the metal/film interface [3]. Recently, some of the present authors have revealed that even on sputter-deposited niobium, free from such inclusions, field crystallization occurs, although the material is less susceptible for field crystallization than that containing inclusions [8]. It has been proposed that air-formed surface

oxide present before anodizing becomes a nucleation site of field crystallization for the inclusions-free niobium [8]. For amorphous anodic niobium oxide, film material is developed simultaneously at the metal/film and film/electrolyte interfaces by migrations of oxygen species inwards and of cations outwards, respectively, through the pre-existing air-formed or thermal oxide. Since the transport number of cations is ~ 0.25 , the nucleation of crystalline oxide should be located at the depth of approximately 25% of the film thickness. This has been supported from the fact that incorporation of electrolyte species deeper than the air-formed oxide region reduces the susceptibility of field crystallization, while the incorporation to the depth less than 25% of the film thickness does not impede the crystallization [8].

Here, we demonstrate the complete suppression of field crystallization of anodic niobium oxide by alloying of niobium with silicon. Even after prior thermal treatment in air, which markedly accelerates the field crystallization of anodic oxide on niobium, no crystalline oxide is developed on the alloy. Further, field crystallization behaviour of the anodic oxide on an Nb-Si layer superimposed on a niobium layer as well as on a niobium layer superimposed on an Nb-Si layer has been examined to elucidate the role of silicon in inhibiting the field crystallization.

2. Experimental

Niobium and Nb-12 at% Si alloy films, approximately 300 nm thick, were prepared by magnetron sputtering on to flat glass substrate as well as electropolished and subsequently anodized high purity aluminium substrate. The niobium film, ~ 40 nm thick, superimposed on Nb-12 at% Si (hereafter denoted as Nb/Nb-Si) as well as the Nb-12 at% Si, ~ 40 nm thick, superimposed on niobium (Nb-Si/Nb) were also prepared. Target used for the preparation of the alloys was 99.9% niobium disk on the sputter erosion region of which silicon plates were

symmetrically placed. The niobium disk without silicon plate was used for the preparation of the niobium films. The silicon content in the alloy was determined using Rutherford backscattering spectroscopy. The structures of the deposited niobium and Nb-12 at% Si films, identified by X-ray diffraction using Cu K α radiation, were bcc and amorphous respectively (Fig. 1). Thus, the Nb-12 at% Si was a single phase alloy containing supersaturated silicon.

Prior to anodizing, some specimens were thermally treated at several temperatures in air for 1.8 ks. The specimens as-deposited and thermally treated were anodized at a constant current density of 50 A m⁻² in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 333 K to 100 V with current decay for 3.6 ks. Surfaces of the anodized specimens were examined by a JEOL JSM-6400F field emission gun scanning electron microscope. Electron transparent sections of the anodized specimens were obtained using a Leica Ultracut S ultramicrotome. Briefly, encapsulated specimens were trimmed initially with glass knives, and suitably thin sections, about 10 nm thick, were prepared using a diamond knife. The sections were observed using a JEOL JEM-2010 transmission electron microscope operating at 200 kV. XPS spectra of the as-deposited and thermally treated Nb-12 at% Si alloy specimens were measured using a Kratos ESCA-3000 system with Mg K α excitation ($h\nu = 1253.6$ eV). Binding energies of the photoelectrons were calibrated by a method described elsewhere [9]. Further, depth profiling analyses of the anodic films were carried out by glow discharge optical emission spectroscopy (GDOES) using a Jobin-Yvon 5000 RF instrument in an argon atmosphere of 898 Pa by applying RF of 13.56 MHz and power of 40 W. Light emissions of characteristic wavelengths were monitored throughout the analysis with a sampling time of 0.01 s to obtain depth profiles. The wavelengths of the spectral lines used were 313.079, 288.158, 249.678 and 130.217 nm for niobium, silicon, boron and oxygen respectively. The signals were detected from a circular area of approximately 4 mm diameter.

3. Results and Discussion

3.1 Field crystallization of anodic oxide on niobium and Nb-Si alloy

Fig. 2(a) shows the voltage-time responses during initial anodizing at a constant density of 50 A m^{-2} to 100 V in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 333 K. the formation voltage increased linearly with time for all the specimens, indicating uniform film growth to 100 V. The slope is larger for the Nb-12 at% Si than that for niobium, mainly due to increased ionic resistivity of the anodic film by incorporation of silicon species. Thermal treatment of the niobium and Nb-12 at% Si increases the voltage surge at the commencement of anodizing, reflecting the increased thickness of pre-formed oxide films. Similar slopes for the as-deposited and thermally treated specimens reveal that the presence of thermal oxide does not change the growth behaviour of anodic oxides on niobium and Nb-12 at% Si.

However, the current transients of niobium during subsequent anodizing at 100 V are highly influenced by the prior thermal treatment (Fig. 2(b)). Immediately after reaching the prescribed formation voltage of 100 V, the current density decreased steeply with time, because of reduction of field strength as a consequence of film growth at a constant voltage. For the as-deposited Nb, the current turns to increase approximately at 1.0 ks, being associated with the development of crystalline oxide in the initially formed amorphous anodic niobium oxide film. In our previous study, the nucleation of crystalline oxide was confirmed at the current minimum, while no crystalline oxide was present during constant current anodizing to 100 V for the as-deposited niobium [10]. The development of crystalline oxide is accelerated by prior thermal treatment of niobium in air; the current minimum appears at shorter anodizing time for the thermally treated specimen. Further, larger current increase is found for the niobium specimens thermally treated at higher temperatures.

In contrast, no current increase occurs for the Nb-12 at% Si alloy, even for the alloy specimen thermally treated at 623 K. The current transients are essentially identical for all the

as-deposited and thermally treated Nb-12 at% Si alloy specimens. The current decreases continuously, following high field kinetics. Thus, the silicon-containing alloy possesses high resistance to field crystallization.

The developments of crystalline oxides in anodic oxide films on the niobium and its absence on the Nb-12 at% Si have been confirmed by scanning electron microscopy. Flaw regions with petal-like morphology, in which crystalline oxide is developed [5, 8, 11], were obvious on the anodic films formed on niobium as-deposited and thermally treated at several temperatures up to 523 K. An example of the surface of the anodic film formed on the niobium thermally treated at 523 K is shown in Fig. 3(a). The number of such flaw regions increased with an increase in the temperature of prior thermal treatment. Thus, thermally formed oxide accelerates the nucleation of crystalline oxide. In contrast to the niobium specimens, surfaces of the anodic films formed on the Nb-12 at% Si alloy were flat and featureless (Fig. 3(b)), indicating no development of crystalline oxide even on the alloy thermally treated in air at 623 K. The thermally formed oxide on the Nb-Si alloy does not accelerate the nucleation of crystalline oxide during film growth.

The effective inhibition of field crystallization of anodic niobium oxide by the addition of silicon to niobium should be partly associated with the modification of air-formed oxide and thermally formed oxide, as can be confirmed by the X-ray photoelectron spectra of the as-deposited and thermally treated Nb-12 at% Si alloy (Fig. 4). The presence of oxidized silicon species is evident from an Si 2p electron peak of 101.8 eV, such that silicon species are incorporated into the air-formed and thermally formed oxide films, modifying the oxide structure. Since the peaks corresponding to metallic niobium and silicon are also detected even after thermal treatment at 523 K, the thickness of the oxide film should be less than 10 nm. The niobium in the oxide films is in pentavalent state, as identified from the Nb 3d spectra with the peak binding energy of Nb3d_{5/2} electron of 207.3 eV (Fig. 4(a)) [12]. The

peak binding energy of 101.8 eV in the Si 2p spectra reveals that the oxidized silicon is in the tetravalent state. Thus, the air-formed and thermally formed oxides consist of a mixture of units of Nb₂O₅ and SiO₂. The amorphous niobium oxide structurally and compositionally modified by the incorporation of silicon species is not easily transformed to the crystalline one.

In addition to the structural and compositional modification of the oxide present before anodizing, continuous incorporation of silicon species into anodic film from substrate should also contribute to the inhibition of crystallization. In fact, it is known that incorporation of electrolyte-derived species into anodic alumina retards electron beam-induced crystallization of the oxide during observation in transmission electron microscopy. Alloying of titanium with aluminium [13], molybdenum [14, 15], silicon [16, 17], tungsten [18, 19] and zirconium [20] enables the growth of amorphous anodic oxide to high voltages at high current efficiency, although an amorphous-to-crystalline transition, occurring on high purity titanium at low voltages of less than 10 V, induces oxygen gas generation and film breakdown. Thus, in order to clarify the roles of the modification of air-formed and thermally formed oxides and the incorporation of silicon species in anodic oxide in inhibiting the crystallization separately, field crystallization behaviour of the anodic oxides formed on the niobium layer superimposed on the Nb-Si layer as well as on the Nb-Si layer superimposed on the niobium layer has been examined.

3.2 Field crystallization of anodic oxide on two-layered Nb/Nb-Si and Nb-Si/Nb

Fig. 5 shows the voltage-time responses of the Nb-Si/Nb and Nb/Nb-Si during anodizing at a constant current density of 50 A m⁻² in the ammonium pentaborate electrolyte at 333 K. For both the as-deposited specimens, the voltage increases linearly with anodizing time, but the slope changes from 1.48 to 1.28 V s⁻¹ at 65 V and from 1.48 to 1.27 V s⁻¹ at 52 V for the

Nb-Si/Nb and the Nb/Nb-Si respectively. The former specimen shows reduction in slope above ~65 V, while the slope increased at ~52 V for the latter specimen. From the voltage at which the slope changes, one can see when the outer layer of niobium or Nb-12 at% Si is totally consumed by anodizing. For instance, for the Nb/Nb-Si, the outer niobium layer is consumed by anodizing to ~52 V, forming a silicon-free anodic oxide. Further anodizing to higher voltage develops a silicon-containing anodic oxide due to oxidation of the Nb-Si layer at the ally/film interface. The higher slope during anodizing of the outer Nb-12 at% Si in the Nb-Si/Nb compared with that of the outer niobium in the Nb/Nb-Si is mainly associated with the increased ionic resistivity of anodic oxide by incorporation of silicon species [21]. Assuming the formation ratio of 2.6 nm V⁻¹ for anodic niobium oxide [22] and the Pilling-Bedworth ratio of 2.6 for Nb/Nb₂O₅ [23], the thickness of the outer niobium layer in the Nb/Nb-Si is estimated to be 52 nm. Since the anodizing time required to consume the outer layer in the Nb-Si/Nb is similar to that in the Nb/Nb-Si, the outer Nb-12 at% Si layer in the Nb-Si/Nb should have a similar thickness to the outer niobium layer in the Nb/Nb-Si.

Two linear regions also appear for the thermally treated Nb-Si/Nb, with each slope being similar to the respective slope for the as-deposited Nb-Si/Nb. A large voltage surge of 14 V appears for the thermally treated Nb-Si/Nb, but the formation voltage, at which the slope changes, is similar to that for the as-deposited one. In contrast, thermal treatment of the Nb/Nb-Si changes the slopes, as in Fig. 5, in addition to the significant voltage surge of 33 V at the commencement of anodizing, suggesting some change in film structure during anodizing to 100 V. The development of crystalline oxide during anodizing to 100 V was found by TEM observation as shown later.

The depth distribution of silicon species in the anodic films formed to 100 V on the as-deposited Nb/Nb-Si and Nb-Si/Nb has been examined by GDOES depth profiling analysis (Fig. 6). In Fig. 6, a wavy profile of niobium in the anodic films is artefact and arises from

light emitted from the respective element. For the Nb-Si/Nb, the silicon species are present only in the intermediate region of the film thickness; the outer 25% and inner 38% of the film thickness is practically free from silicon species. The outer silicon-free layer is formed since the silicon species are immobile; only niobium ions migrate outwards, developing a new film material at the film/electrolyte interface. Thus, the silicon species are present in the film region where the film material is formed at the metal/film interface. However, after the consumption of the outer Nb-Si layer, no further incorporation of silicon species occurs during anodizing of the inner niobium layer, developing the silicon-free inner oxide layer. Since immobile silicon species can be used as a marker, the transport number of cations in this anodic oxide is estimated to be approximately 0.25, from the thickness of the outer silicon-free layer relative to the total film thickness. This value is in agreement with the previous reports [22, 23].

Since the anodic oxide is formed both at the metal/film and the film/electrolyte interfaces by simultaneous migration of O^{2-}/OH^- ions inwards and niobium ions outwards respectively through the pre-existing air-formed oxide, the air-formed oxide should be located at the depth of ~25% of film thickness, which is shown as a marker plane in Fig. 6(a). This region is still contaminated with silicon species since the silicon species are immobile during film growth. In contrast, the anodic film formed on the Nb/Nb-Si contains silicon species only in the inner 33% of the film thickness (Fig. 6(b)). The air-formed oxide region (the marker plane) is not contaminated with silicon species in this case. Boron species are also incorporated into the anodic films formed on the Nb-Si/Nb and Nb/Nb-Si, but the incorporation depth is only ~10%. The shallow depth distribution of the boron species is owing to their outer migration in growing anodic niobium oxide [21, 25]. The increased intensity of the boron signal at the substrate and the relatively high background in the oxide arise due to overlapping of light emitted from niobium (249.697 nm) with the measured boron line (249.678 nm) [24].

Scattered oxygen signal is due to low sensitivity for oxygen, and relatively high background of oxygen in metal substrate may be caused by the presence of oxygen in analytical chamber, since ultra-high vacuum is not used in GDOES depth profiling analysis.

As confirmed by GDOES depth profiling analysis in Fig. 6, depth distributions of silicon species in the Nb-Si/Nb and Nb/Nb-Si are different, causing different crystallization behaviour of anodic oxide. Fig. 7(a) shows the current transients during anodizing of the Nb-Si/Nb as-deposited and thermally treated at 623 K. Compared with the as-deposited niobium, the current increase due to crystallization is markedly suppressed for the Nb-Si/Nb. The thermally treated Nb-Si/Nb reveals similar current transient to the as-deposited one, although the thermal treatment of the niobium film increased significantly the current density as in Fig. 2. Both the as-deposited and thermally treated Nb-Si/Nb reveal slight current increase after ~2.5 ks, indicating that field crystallization is not totally avoided.

The current transients of the Nb/Nb-Si (Fig. 7(b)) are different from those of the Nb-Si/Nb. The current density of the as-deposited Nb/Nb-Si decreases continuously. The current transient of the specimen thermally treated at 523 K is almost the same as that of the as-deposited one. Apparently, field crystallization is effectively inhibited. Slightly higher current density is observed for the specimen thermally treated at 573, compared with that of the as-deposited one, after anodizing for 400 s. Further increase in the temperature of thermal treatment up to 623 K results in a marked increase in the current density. The current increase for the specimen thermally treated at 623 K occurs soon after the commencement of constant voltage anodizing. The current increase is terminated within a relatively short period of time, then the current decreases continuously.

Such different current transients of the Nb-Si/Nb and Nb/Nb-Si specimens are associated with the different behaviours of nucleation and growth of crystalline oxide during anodizing. Fig. 8 shows the scanning electron micrographs of the surfaces of the as-deposited niobium

(Fig. 8(a), the Nb-Si/Nb (Figs. 8(b)-(c)) and the Nb/Nb-Si (Figs. 8(d)-(f)) after anodizing for 3.6 ks. The petal-like flaw regions are present on the Nb-Si/Nb as-deposited and thermally treated at 623 K (Figs. 8(b)-(c)). However, the number of such regions is markedly reduced, compared with the as-deposited niobium (Fig. 8(a)), suggesting that the presence of silicon species in the air-formed oxide suppresses the nucleation of crystalline oxide. Since the sizes of the flaw regions are comparable between the niobium and the Nb-Si/Nb specimens (10~30 μm in diameter), growth of crystalline oxide is not influenced by the presence of silicon species in the intermediate depth region of the anodic film.

The surface of the as-deposited Nb/Nb-Si is smooth after anodizing, and no flaw regions with petal-like morphology are observed in Fig. 8(d). Careful observations of the entire surface of the specimen revealed that a tiny number of the flaw regions were present in the anodic film. With increasing thermal treatment temperature, the number of the flaw regions increases largely as in Figs. 8(d)-(f), and for the specimen thermally treated at 623 K, the entire surface is covered almost totally with a number of small flaw regions. Compared with the as-deposited niobium and the Nb-Si/Nb, the size of a flaw region on the Nb/Nb-Si is small, being less than 1 μm . The accelerated nucleation of crystalline oxide by thermal treatment of the Nb/Nb-Si is due to the absence of silicon species in the air-formed oxide, but the growth of crystalline oxide is suppressed by continuous incorporation of silicon species from the metal/film interface into the anodic film.

Through the examinations of the crystallization behaviours of the Nb-Si/Nb and Nb/Nb-Si specimens, the different roles of silicon species in the air-formed oxide and in the anodic oxide are disclosed. The thermally formed oxide without silicon species is transformed easily to the crystalline oxide during anodizing, particularly when the thermal treatment temperature increases. The modification of air-formed oxide by silicon species is effective in impeding the nucleation of crystalline oxide even after thermal treatment. However, once the crystalline

oxide is nucleated, the growth of crystalline oxide occurs at a similar rate to that in the anodic film on niobium. In contrast, the incorporation of silicon species into the anodic film from the metal/film interface under the situation where the silicon species are absent in the air-formed or thermally formed oxides hinders the growth of crystalline oxide, although the nucleation is not influenced by the silicon species.

The findings support our previously proposed mechanism that the crystalline oxide in the anodic films on the inclusion-free niobium substrate is nucleated at the air-formed oxide region. The TEM observations of the Nb/Nb-Si specimens have further ensured this mechanism. The voltage-time curve of the Nb/Nb-Si thermally treated at 623 K (Fig. 5) revealed a probable structural change in the anodic oxide during anodizing. At the commencement of anodizing the voltage jump occurs to 33 V, reflecting the formation of relative thick thermal oxide. The TEM observation of an ultramicrotomed section of the thermally treated specimen (Fig. 9(a)) reveals that the thickness of the oxide film is ~88 nm. The thermal oxide is amorphous as evident from a diffuse halo ring in the selected area electron diffraction pattern. In anodizing to 100 V, it is evident from Fig. 9 (b) that crystalline oxide is developed in the anodic film. The crystalline oxide is present in the middle of the outer silicon-free oxide layer, not at the film region adjacent to the metal/film interface or to the film/electrolyte interface. During anodizing, new film materials are formed both at the film/electrolyte and metal/film interfaces. The presence of the crystalline oxide in the middle depth of the anodic film clearly demonstrates that the thermal oxide becomes a nucleation site for field crystallization. Since the initial slope of the thermally treated Nb/Nb-Si in Fig. 5 is different from that of the as-deposited Nb/Nb-Si, the structural transformation may occur at an early stage of anodizing. When silicon species are present in the air-formed or thermal oxides, the transformation of the amorphous air-formed or thermal oxides to crystalline oxide is impeded since the silicon oxide is a well known glass former.

4. Conclusions

Field crystallization behaviours of anodic niobium oxide has been examined using magnetron sputtered niobium and Nb-12 at% Si alloy. To elucidate the role of silicon species influencing the crystallization behaviour, two-layered films comprising a niobium layer superimposed on an Nb-12 at% Si layer as well as a Nb-12 at% Si layer superimposed on a niobium layer have been anodized. From current transients during anodizing of these specimens and characterization of the anodic films developed, the following conclusions are drawn.

- 1) Magnetron sputtered Nb-12 at% Si alloy forms uniform amorphous oxide at 100 V in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 333 K, although crystalline anodic oxide is developed in the anodic film formed on high purity niobium under the same condition. Prior thermal treatment of the niobium accelerates the crystallization, but no crystalline oxide is developed for the Nb-12 at% Si alloy even after thermal treatment at 623 K.
- 2) Field crystallization occurs in the middle depth of the anodic niobium oxide, since the air-formed or thermal oxide becomes a nucleation site for field crystallization. The modification of the air-formed and thermal oxides by silicon species impedes the nucleation of crystalline oxide. However, modification of the pre-existing oxide does not change the growth of crystalline oxide.
- 3) Growth of the crystalline oxide during anodizing is suppressed by continuous incorporation of silicon species from the metal/film interface, since silicon-containing innermost amorphous oxide layer does not transform easily to the crystalline oxide, even if the outer part of the film materials is crystallized.
- 4) Thus, as a consequence of the modification of an air-formed or thermal oxide as well as the incorporation of silicon species in the inner part of the anodic film, the anodic film formed on the Nb-12 at% Si alloy is highly resistant against field crystallization.

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Figure captions

Fig. 1 X-ray diffraction patterns of the sputter-deposited niobium and Nb-12 at% Si alloy on glass substrate.

Fig. 2 (a) Voltage-time responses and (b) current transients of the sputter-deposited niobium and Nb-12 at% Si alloy during anodizing at 100 V in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 333 K for 3.6 ks. Initially, a constant current density of 50 A m⁻² was applied to reach the formation voltage of 100 V.

Fig. 3 Scanning electron micrographs of surfaces of the sputter-deposited (a) niobium thermally treated at 523 K and (b) Nb-12 at% Si alloy thermally treated at 623 K after anodizing at 100 V in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 333 K for 3.6 ks.

Fig. 4 (a) Nb 3d and (b) Si 2p XPS spectra of the Nb-12 at% Si alloy as-deposited and thermally treated at 523 K

Fig. 5 Voltage-time curves of the as-deposited and thermally treated Nb- 12 at% Si / Nb and Nb / Nb-12 at% Si specimens during anodizing at 50 A m⁻² to 100 V in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 333 K.

Fig. 6 GDOES depth profiles of the anodic films formed at 50 A m⁻² to 100 V on the (a) Nb-12 at% Si / Nb and (b) Nb / Nb-12 at% Si in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 333 K.

Fig.7 Current transients of (a) the Nb-12 at% Si / Nb as-deposited and thermally treated at 623 K and (b) the Nb / Nb-12 at% Si as-deposited and thermally treated at 523-623 K during anodizing at 100 V in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 333 K.

Fig. 8 Scanning electron micrographs of surfaces of the specimens anodized at 100 V in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 333 K for 3.6 ks; (a) as-deposited niobium, the Nb-12 at% Si / Nb (b) as-deposited and (c) thermally treated at 623 K and

the Nb / Nb-12 at% Si (d) as-deposited and thermally treated at (e) 573 and (f) 623 K.

Fig. 9 Transmission electron micrographs of ultramicrotomed sections of the Nb / Nb-12 at% Si: (a) after thermal treatment at 623 K, (b) after thermal treatment at 623 K and subsequently anodized to 100 V at a constant current density of 50 A m^{-2} in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 333 K.

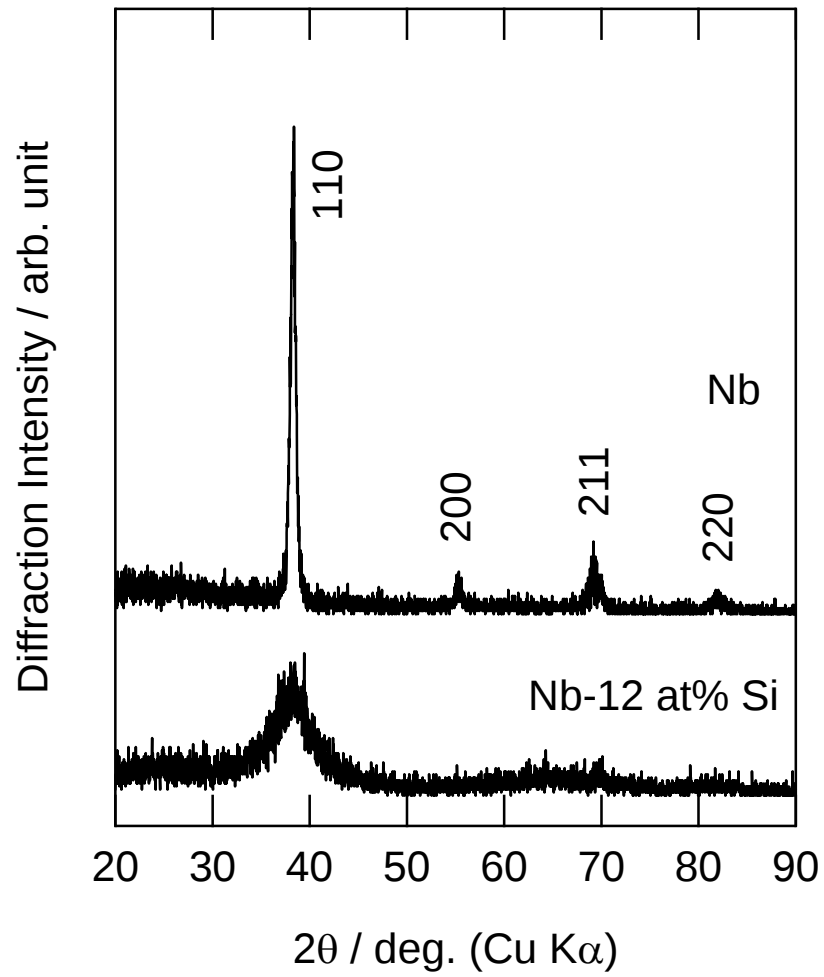


Fig. 1 X-ray diffraction patterns of the sputter-deposited niobium and Nb-12 at% Si alloy on glass substrate.

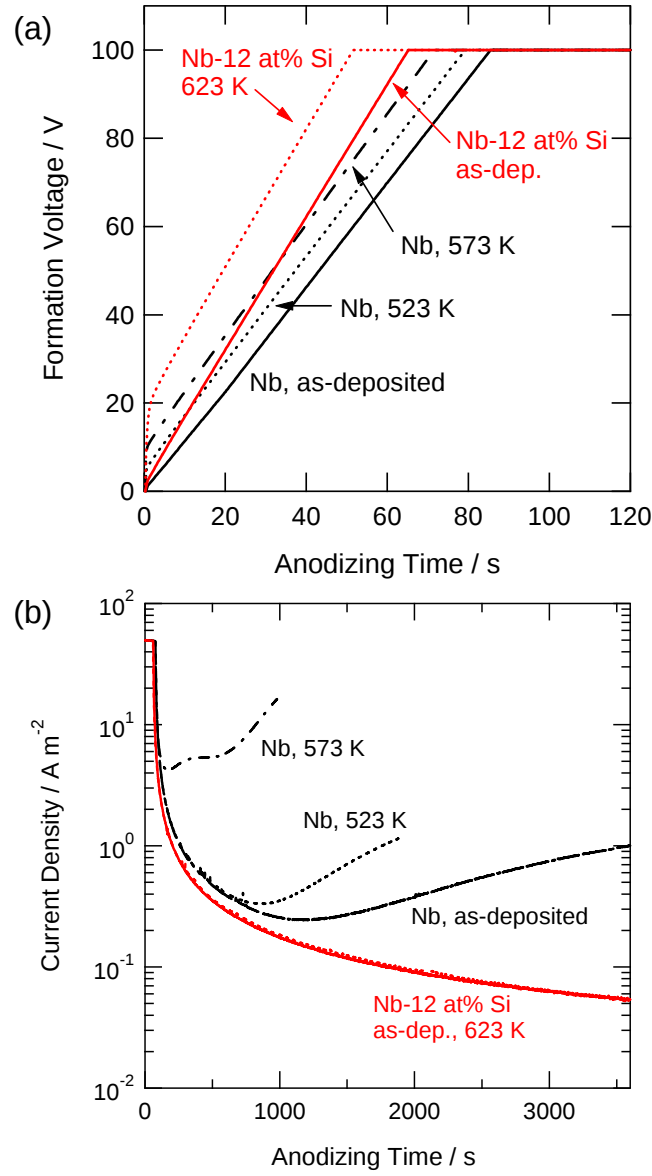


Fig. 2 (a) Voltage-time responses and (b) current transients of the sputter-deposited niobium and Nb-12 at% Si alloy during anodizing at 100 V in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 333 K for 3.6 ks. Initially, a constant current density of 50 A m⁻² was applied to reach the formation voltage of 100 V.

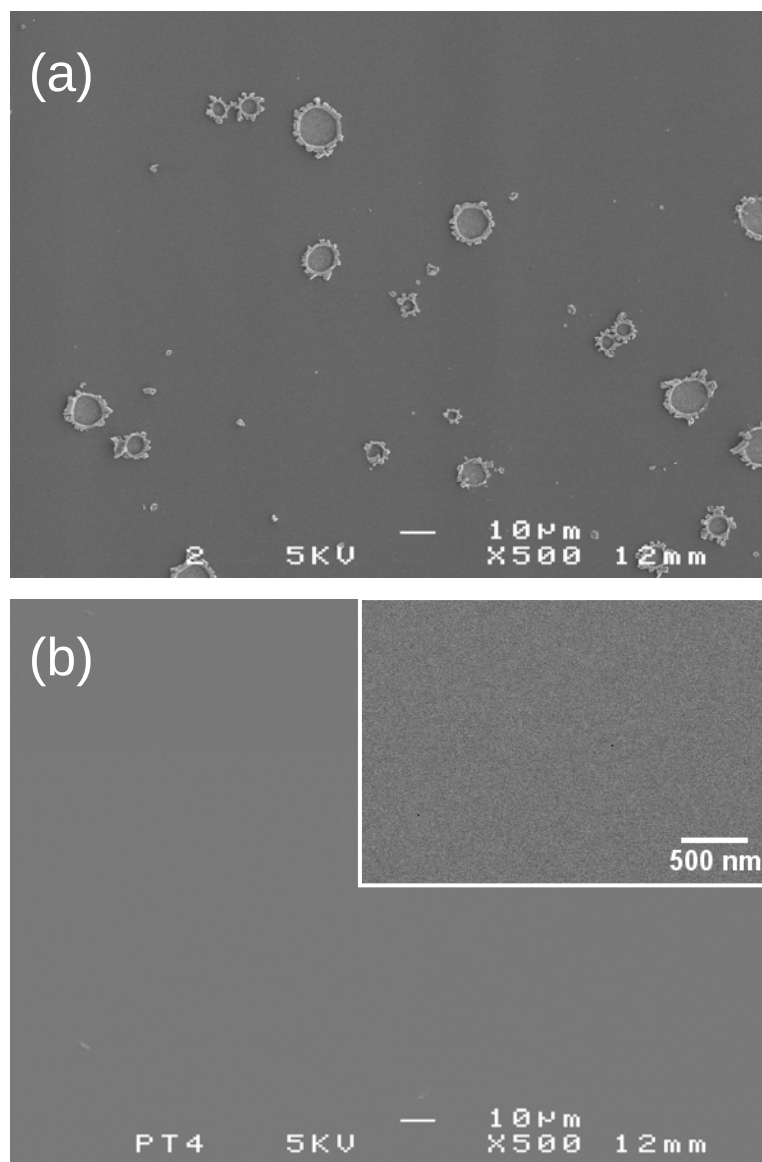


Fig. 3 Scanning electron micrographs of surfaces of the sputter-deposited (a) niobium thermally treated at 523 K and (b) Nb-12 at% Si alloy thermally treated at 623 K after anodizing at 100 V in in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 333 K for 3.6 ks.

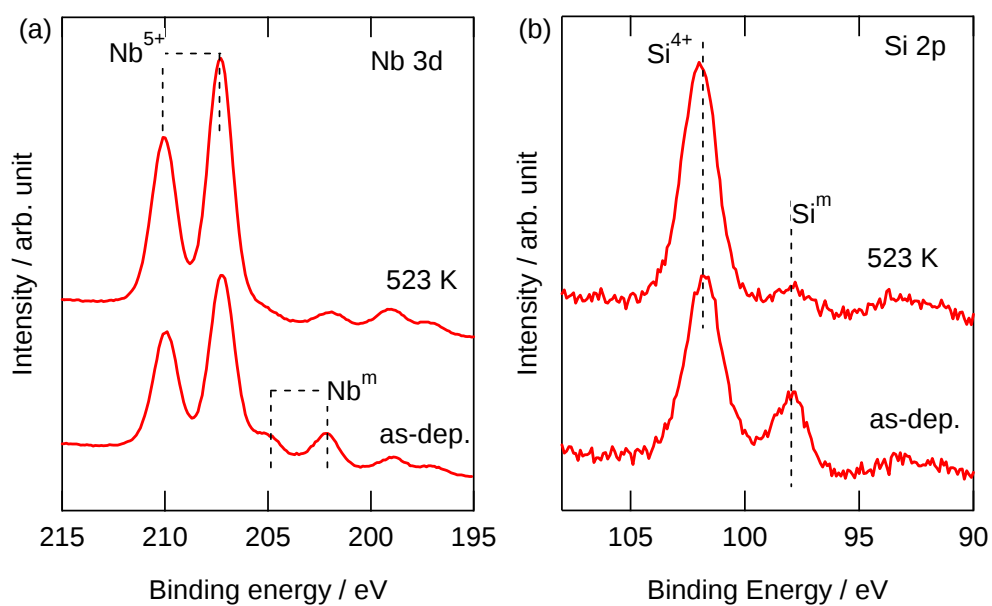


Fig. 4 (a) Nb 3d and (b) Si 2p XPS spectra of the Nb-12 at% Si alloy as-deposited and thermally treated at 523 K

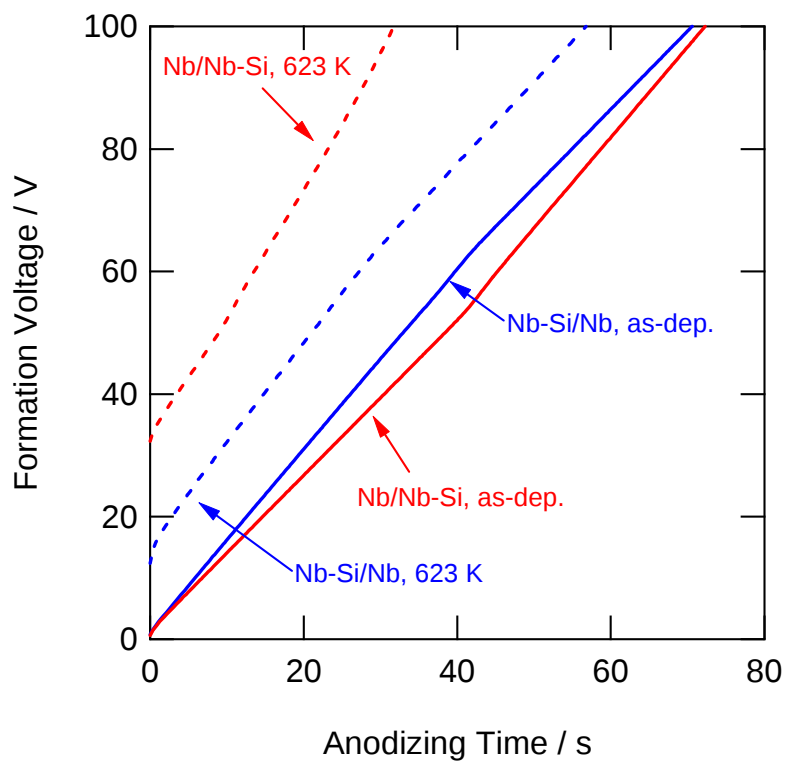


Fig. 5 Voltage-time curves of the as-deposited and thermally treated Nb- 12 at% Si / Nb and Nb / Nb-12 at% Si specimens during anodizing at 50 A m^{-2} to 100 V in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 333 K.

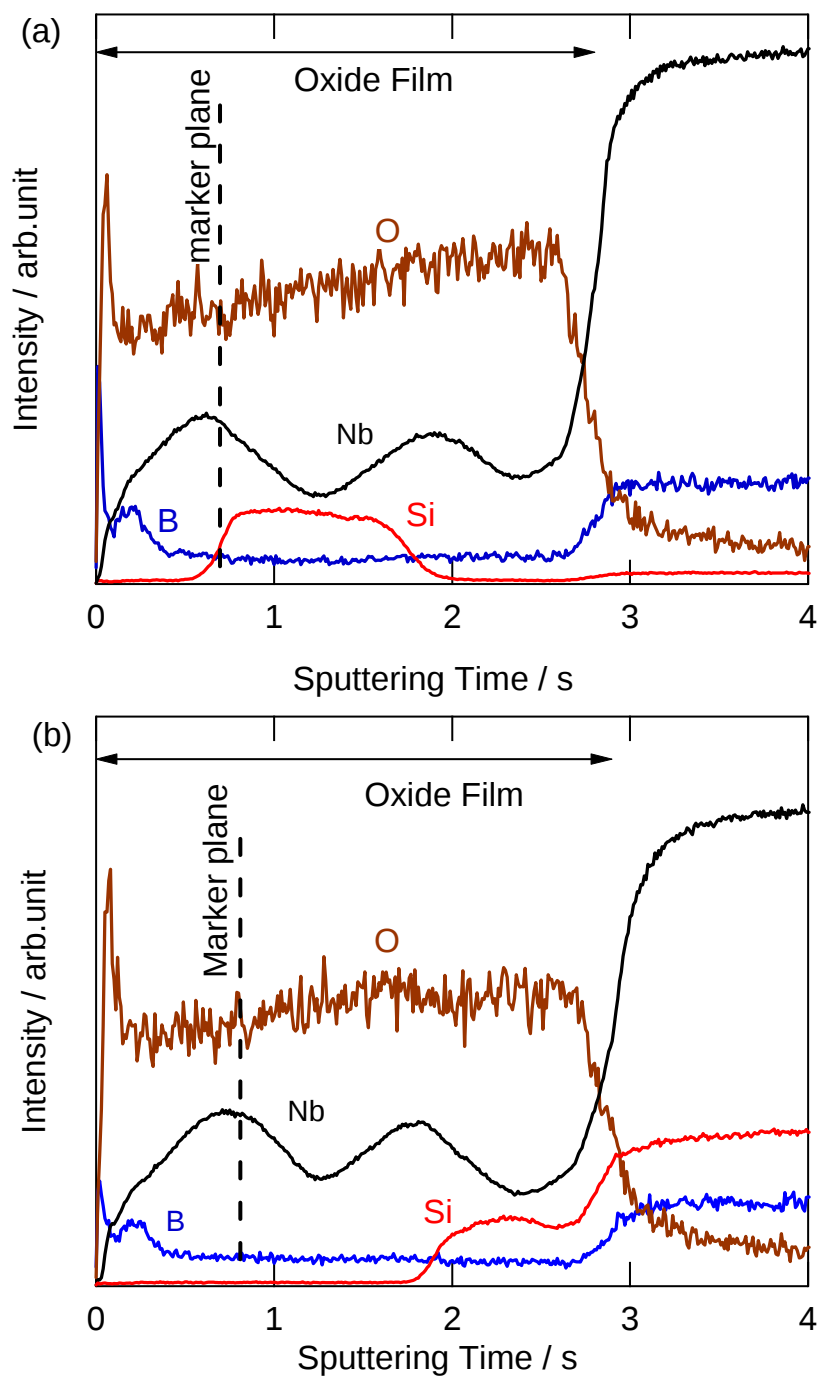


Fig. 6 GDOES depth profiles of the anodic films formed at 50 A m^{-2} to 100 V on the (a) Nb-12 at% Si / Nb and (b) Nb / Nb-12 at% Si in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 333 K.

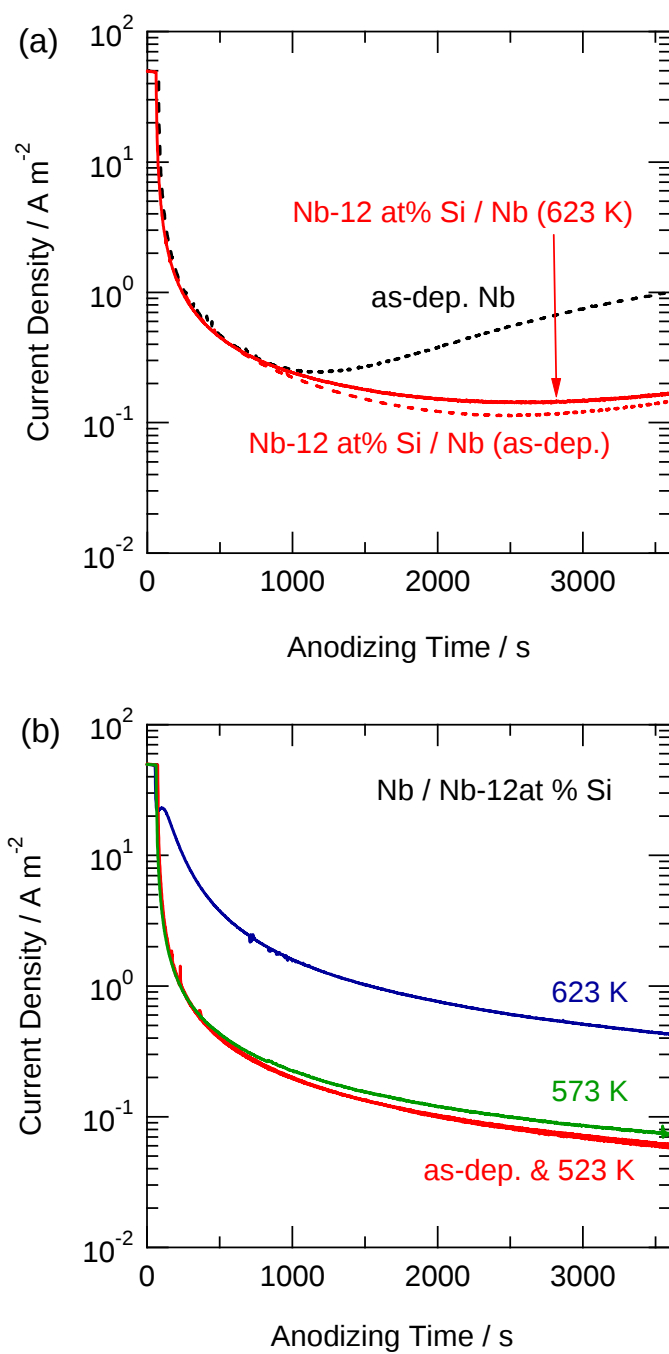


Fig.7 Current transients of (a) the Nb-12 at% Si / Nb as-deposited and thermally treated at 623 K and (b) the Nb / Nb-12 at% Si as-deposited and thermally treated at 523-623 K during anodizing at 100 V in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 333 K.

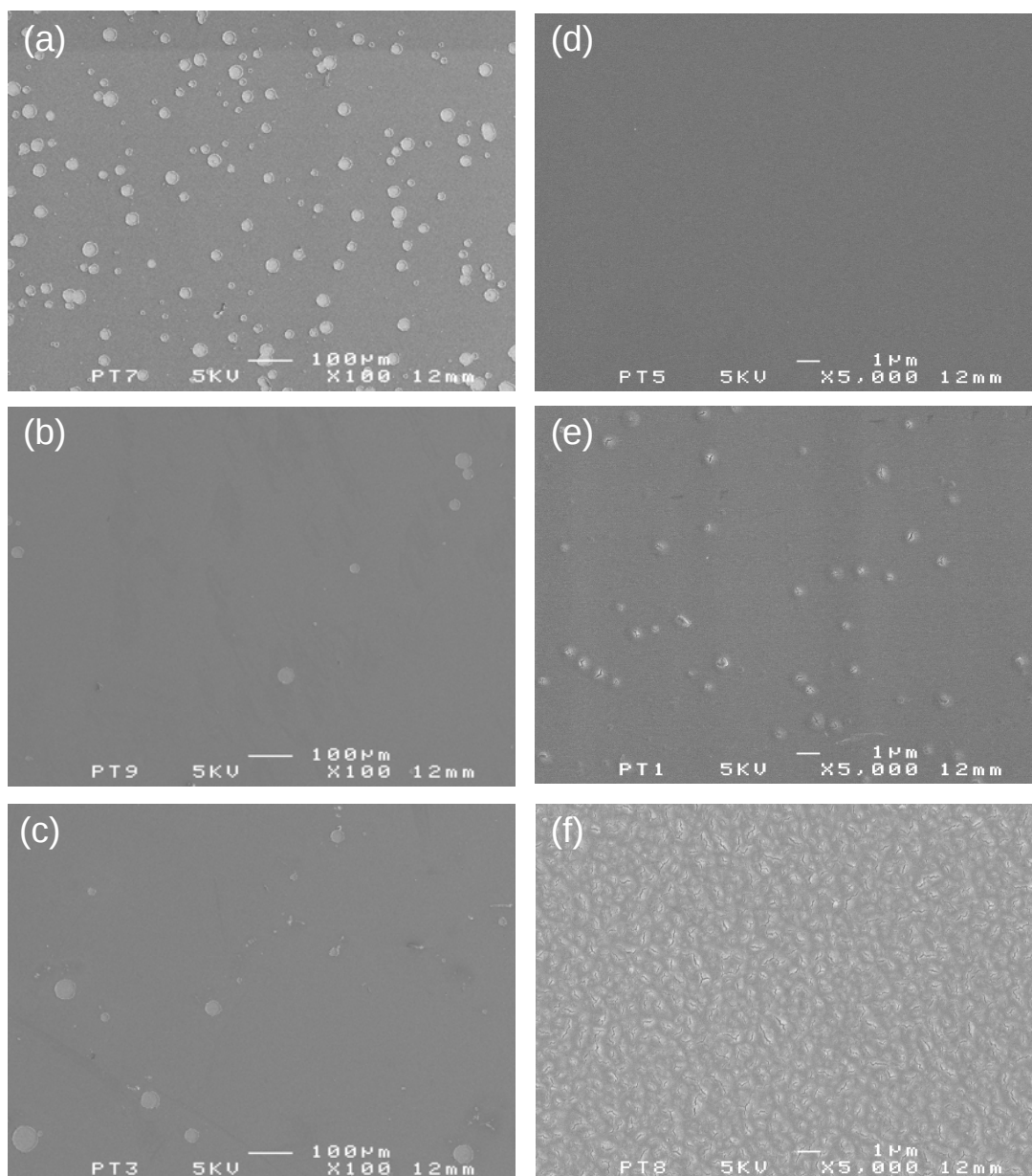


Fig. 8 Scanning electron micrographs of surfaces of the specimens anodized at 100 V in 0.1 mol dm⁻³ ammonium pentaborate electrolyte at 333 K for 3.6 ks; (a) as-deposited niobium, the Nb-12 at% Si / Nb (b) as-deposited and (c) thermally treated at 623 K and the Nb / Nb-12 at% Si (d) as-deposited and thermally treated at (e) 573 and (f) 623 K.

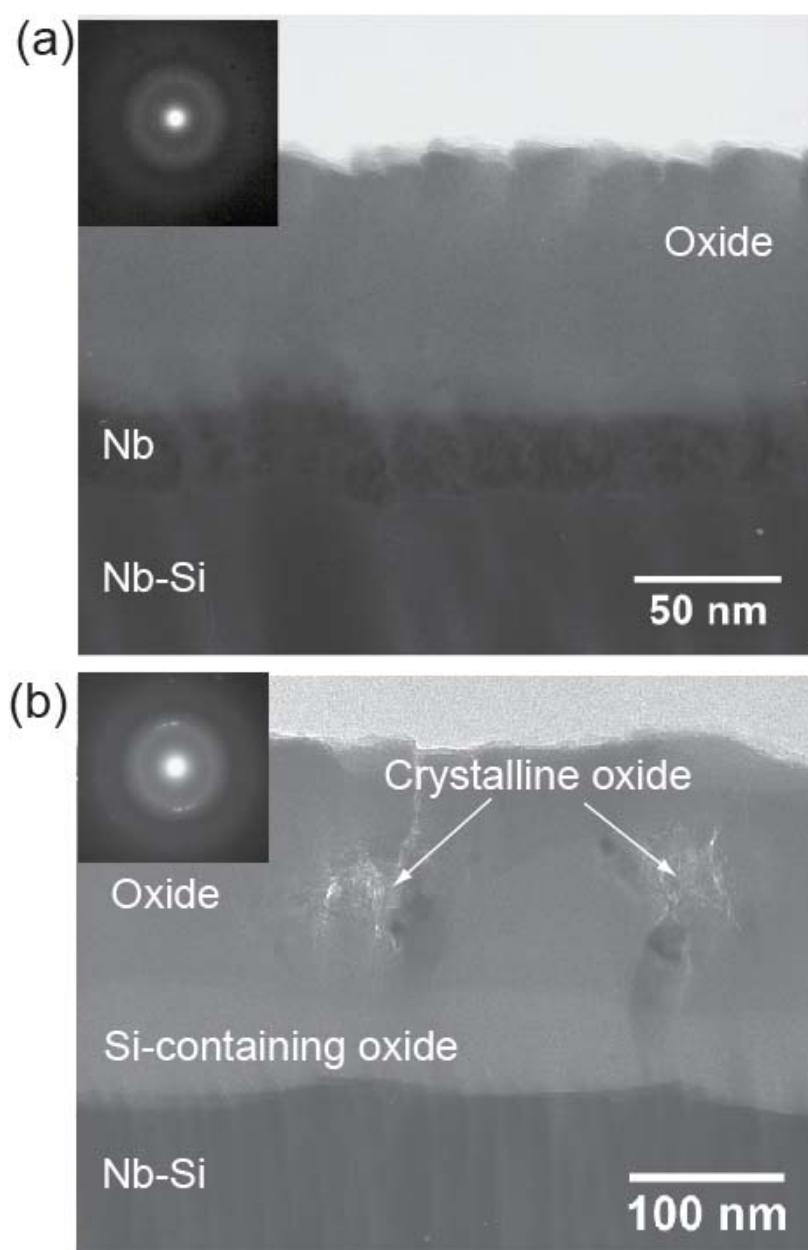


Fig. 9 Transmission electron micrographs of ultramicrotomed sections of the Nb / Nb-12 at% Si: (a) after thermal treatment at 623 K, (b) after thermal treatment at 623 K and subsequently anodized to 100 V at a constant current density of 50 A m^{-2} in 0.1 mol dm^{-3} ammonium pentaborate electrolyte at 333 K.