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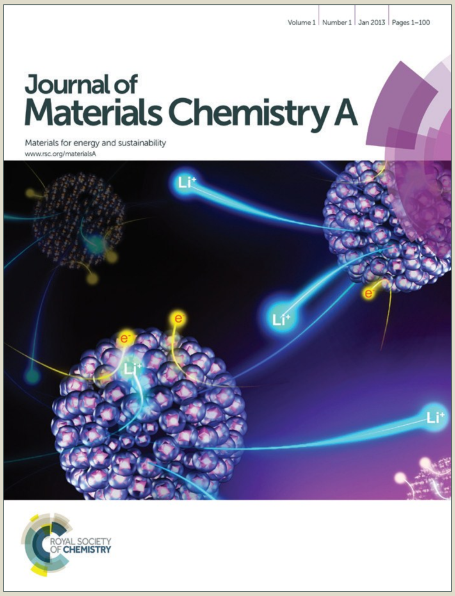

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Novel Flux Coating Method for Fabrication of Layer of Visible-Light-Responsive Ta_3N_5 Crystals on Tantalum Substrate

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ABSTRACT

Layers of well-developed crystals of Ta_3N_5 were successfully fabricated on Ta substrates by a novel flux coating method in a flow of NH_3. The flux coating method is a simple one: the Ta substrates were coated with aqueous solutions of sodium compounds (= fluxes) and subsequently heated in a flow of NH_3, whereupon the surfaces of the Ta substrates were dissolved in the flux, resulting in Ta_3N_5 crystal layers. The Ta in the Ta_3N_5 was provided by the substrate. Therefore, crystal layers with good adhesion could be grown directly on the substrates. The shape of the individual crystals as well as the surface morphology of the layers formed was determined by the flux used. The crystals fabricated using NaCl-Na_2CO_3 as the flux were prismatic and had relatively smooth faces, covering the surface of the Ta substrate uniformly. The crystal growth field resulting from the use of this method yielded well-formed crystals, which presumably grew from a solution. Finally, it was confirmed that a thus-synthesized Ta_3N_5 crystal layer modified using Co-Pi as the cocatalyst generated a photoanodic current under visible-light irradiation.

Introduction

As hydrogen gains importance as a source of clean energy, transition metal (oxy)nitrides are increasingly receiving attention as visible-light-sensitive materials for the photocatalytic and photoelectrochemical splitting of water.[1-4] Materials capable of absorbing visible light allow for the use of solar energy as an energy source. Hydrogen can be regarded as a source of genuine clean energy, if it is produced from water using sunlight and semiconductor photocatalysts and not fossil fuels. Among the various metal (oxy)nitrides used as catalysts for the synthesis of hydrogen, tantalum nitride (Ta_3N_5) has a band gap suitable for splitting water. Further, the narrowness of its band gap (2.1 eV) allows for the absorption of visible light with wavelengths of up to 600 nm.[5,6] In the past five years, Ta_3N_5 films have been used for the oxidation of water.[7-13] Ta_3N_5 powders and thin films (or photoanodes) are conventionally prepared by the nitridation of precursor powders and thin oxide films (mostly of Ta_2O_5) at relatively high temperatures in an NH_3 flow.[5,6,11-15]

We had previously reported the fabrication of crystal layers of various oxides and fluorides using a flux coating method.[16-20] Flux method is one of the crystal growth technique from high temperature solutions and allows for the fabrication of highly crystalline, idiomorphic crystals.[21-24] In the case of conventional flux-based crystal growth methods, the raw material (solute) and the flux (both in powder form) are placed in a suitable crucible. In contrast, in the proposed method, the raw materials are coated on the surface of the appropriate substrate in the form of a paste or an aqueous solution. When the substrate is heated, the flux components melt and dissolve the solute, resulting in the growth of crystals on the substrate surface. In some cases, the substrate can also be used as a source of raw materials. For instance, a layer of $NaTaO_3$ crystals could be fabricated using a piece of Ta foil both as the substrate and the Ta source.[17] Moreover, we demonstrated that these $NaTaO_3$ crystals could be transformed into those of Ta_3N_5 by nitridation in an NH_3 flow.[17] However, the cubic $NaTaO_3$ single crystals constituting the layer became cubic, polycrystalline Ta_3N_5, owing to changes in the crystal structure. The pores observed on the thus-fabricated particles were owing to the nitridation of Ta_2O_5 into Ta_3N_5.[25]

On the basis of these results, we devised a novel flux coating method for synthesizing layers of nitride crystals. We employed this method for the direct fabrication of Ta_3N_5 crystal layers on Ta substrates. A part of the surface of the Ta substrate could be converted into well-formed crystals. To ensure the fabrication of well-formed Ta_3N_5 crystals, the correct flux must be used. The surface of the Ta substrate should be dissolved by the flux and undergo crystallization. In addition, the flux should be reacted with Ta to form a precursor phase, because Ta_3N_5 cannot be produced by simply heating Ta; however, the precursor phase should be a temporary one. Moreover, the flux should be highly soluble in water, because an aqueous solution of the flux can be readily coated on hydrophilized substrates before they are heated. Further, any residual flux can be removed readily after heating. Given these facts, we first used sodium compounds as fluxes, because it is known that $NaTaO_3$ can be nitrided into Ta_3N_5 even if the $NaTaO_3$ phase is formed by a reaction between the Ta surface and a Na compound (*i.e.*, the flux).

Experimental

As mentioned above, in this study, layers of Ta_3N_5 crystals were fabricated by a novel flux coating method. Ta foil was used as both the substrate and the Ta source, and the nitrogen part of Ta_3N_5 came from the NH_3 gas used. Reagent-grade $NaNO_3$, NaCl, and Na_2CO_3 powders were used as the fluxes. First, the Na compounds (*i.e.*, fluxes) were dissolved in distilled water to form solutions. The typical fabrication conditions are listed in Table 1. Next, 10 or 5 μL of the aqueous solutions was placed on the Ta substrates (10 × 15 × 0.1 mm), which had been dry-cleaned and hydrophilized by being irradiated under vacuum-ultraviolet light (λ = 172 nm) from a xenon excimer lamp

(UER172-200, Ushio Inc.). The solution-coated substrates were dried in an electric oven at 100 °C for 30 min. Next, the substrates were put in an alumina boat, which was placed at the center of a horizontal alumina tube furnace (diameter = 24 mm). The substrates were then heated to 700–850 °C at a rate of 10 $°C \cdot min^{-1}$ and held at this temperature for 0 or 1 h in an NH_3 flow to effect ammonolysis. The NH_3 flow rate was maintained at 100 $mL \cdot min^{-1}$. Subsequently, the substrates were allowed to cool to 300 °C and then to room temperature inside the furnace in NH_3 and N_2 flows, respectively. The Ta_3N_5-coated substrates were then immersed in warm water to remove any residual flux. Next, any grown crystals exhibiting weak adhesion to the substrate surface were removed in water through weak sonication (US-104, 150 W, 38 kHz, SND Co., Ltd.).

The fabricated crystal layers were observed using scanning electron microscopy (SEM; JEOL, JCM-5700) and field-emission scanning electron microscopy (FESEM; JEOL, JSM-7600F). The crystal phases were studied using X-ray diffraction (XRD; Rigaku, MiniflexII). The ultraviolet-visible (UV-vis) absorption spectra of the crystal layers were obtained using a spectrophotometer (JASCO, V-670). The photoelectrochemical (PEC) properties of the Ta_3N_5 crystal layers were investigated using a three-electrode setup in an Ar atmosphere. Before the PEC measurements, the Ta_3N_5 crystal layers were modified using cobalt phosphate (Co-Pi) as a cocatalyst, which was electrochemically coated onto the Ta_3N_5 crystal layers using a 0.5 mM solution of $Co(NO_3)_2$ in a potassium phosphate buffer. The fabricated Co-Pi/Ta_3N_5/Ta photoelectrode, an Ag/AgCl electrode, and a Pt wire were connected to a potentiostat and used as the working, reference, and counter electrodes, respectively. The electrolyte solution used was a 0.2 M aqueous Na_2SO_4 solution, whose pH value was adjusted to 13 using NaOH. The photoelectrode was irradiated using a 300 W Xe lamp equipped with a cut-off filter ($\lambda > 420$ nm).

Results and Discussion

Fabrication of Ta_3N_5 crystal layers using various fluxes

First, crystal layers were fabricated using various Na compounds as fluxes at a holding temperature of 850 °C and a holding time of 1 h. Fig. S1 shows digital photographs of the surfaces of the Ta substrates after the fabrication of the crystal layers and subsequent ultrasonication for 30 min. As can be seen from the digital photographs, layers of red crystals were formed for all fluxes; the exception was NaCl (Run No. 3). That the substrate surface color was dark red indicates that a large number of Ta_3N_5 crystals were formed. Considering that Ta_3N_5 cannot be synthesized by simply heating Ta in an NH_3 flow, it is likely that the Na compounds dissolved the surfaces of the Ta substrates, resulting in the formation of precursor materials for Ta_3N_5. On the other hand, NaCl exhibited a low reactivity with respect to the Ta surface, since the color of the substrate surface in this case was similar to that of a Ta substrate heated in an NH_3 flow (Fig. S1c). In addition, when 5 μL of NaCl-Na_2CO_3 was used, the entire substrate surface turned light red (Run No. 5, Fig. S1e). Further, the crystal layer exhibited good adhesion to the substrate surface, because almost no crystals were removed during ultrasonication. However, the other crystal layers exhibited inhomogeneities in the surface color along the plane of the substrate surface. This indicates that the melts of the Na compounds used as the fluxes for these crystal layers did not cover the entire surface of the Ta substrate. In the cases when Na_2CO_3 and 10 μL of NaCl-Na_2CO_3 were used as the fluxes, numerous red crystals were formed; however, some of them were removed during ultrasonication, because they exhibited poor adhesion to the substrate, resulting in the observed inhomogeneities in the surface color.

Fig. 1 shows SEM images of the surfaces of the Ta_3N_5 crystal layers formed on the Ta substrates. When the crystal layer was fabricated using $NaNO_3$ as the flux, polyhedron crystals less than ~1 μm in size were observed; further, numerous pores were present on the surfaces of these crystals (Fig. S2a and 1a). The crystal layer fabricated using Na_2CO_3 as the flux consisted of well-formed prismatic crystals (marked area in Fig. S1b, Fig. S2b and 1b). When NaCl was used as the flux, prismatic crystals less than 100 nm in width and 500 nm in length grew on the Ta surface (Fig. S2c and 1c). When 10 μL of an aqueous NaCl-Na_2CO_3 solution was used as the flux coating, aggregates of small particles were observed (Fig. S2d), while well-formed prismatic crystals were observed in high-magnification images (Fig. 1d). When the amount of the coating solution used was decreased to 5 μL, well-developed prismatic crystals with relatively smooth faces and angular corners grew on the entire substrate (Fig. 1e and 1f). These prismatic crystals were thought to be single crystals of Ta_3N_5. Finally, the thickness of the crystal layer was approximately 2.1 μm (Fig. S3).

Fig. 2 shows the XRD profiles for the crystal layers fabricated using the various Na compound as fluxes. All the crystal layers exhibited XRD patterns that contained diffraction lines attributable to Ta_3N_5 (○-marked lines), Ta_2N (▲-marked lines),[10,13] and Ta (owing to the substrate, ■-marked lines). When the crystal layers were fabricated using Na_2CO_3 and 10 μL of NaCl-Na_2CO_3 as the fluxes (Run No. 2, 4, respectively), low-intensity diffraction lines corresponding to $NaTaO_3$ were observed (●-marked lines) in addition those corresponding to Ta_3N_5, Ta_2N, and Ta (Fig. 2b and 2d). $NaTaO_3$ was formed by a reaction between Ta and Na_2CO_3 and did not undergo nitridation. When NaCl was used as the flux (Run No. 3), very weak diffraction lines corresponding to Ta_3N_5 were observed at 2θ of 15−38° (Fig. 2c). The small, prismatic crystals observed in the SEM image of the sample (Fig. 1c) were determined to be of Ta_3N_5. The crystal layer fabricated using NaCl-Na_2CO_3 as the flux (Run No. 4, 5) contained an unknown phase (★-marked lines) (Fig. 2d and 2e). The intensities of the corresponding diffraction lines were weaker than those of the lines for Ta_3N_5 (*i.e.*, the target phase) in the case when 5 μL of NaCl-Na_2CO_3 was used as the flux. Thus, the amount of the unknown phase product would be small. On the basis of the digital photographs, SEM images, and XRD patterns of the various samples, we concluded that 5 μL of NaCl-Na_2CO_3 was the best flux for the direct fabrication of a layer of Ta_3N_5 crystals on a Ta substrate.

Next, we discuss the mechanisms of formation of Ta_3N_5 using the various fluxes. For all the fluxes, the Ta_3N_5 crystals were formed by the dissolution of the surface of the Ta substrate by the flux used and a subsequent reaction between the dissolved Ta and the flux. Considering that the Ta and N sources for Ta_3N_5 were the Ta substrate and NH_3 gas, respectively, the Na compounds (*i.e.*, fluxes) coated on the surface of the Ta substrate might seem unnecessary. However, as mentioned previously, Ta_3N_5 cannot be produced by simply heating Ta metal in an NH_3 flow.[17,26] Therefore, it is likely that the Ta_3N_5 crystals were formed via precursor materials that were produced by a reaction between the Ta from the substrate surface and the flux used. Compounds related to the Ta-O, Na-Ta-O, and Ta-Cl systems, such as Ta_2O_5 and $NaTaO_3$, are probably the precursor materials formed. Ta_2O_5 is conventionally used as a precursor oxide for Ta_3N_5; however, it is difficult to synthesize Ta_2O_5 owing to the fact that the flux used (*i.e.*, the oxygen source) is present in a small amount and given that the NH_3 gas used is usually of high purity. Therefore, it is probable that other tantalum oxides (TaO_x ($x < 5/2$)) are the precursor materials for Ta_3N_5. In addition, we had previously reported that Ta_3N_5 can be produced by heating $NaTaO_3$ in an NH_3 flow.[17] In the present study, $NaTaO_3$ or phases related to the Na-Ta-O system could be produced by reacting TaO_x and Na_2CO_3 (as flux); this was proven by the results of the XRD analysis. Further, most of these compounds were transformed into Ta_3N_5. On the other hand, when NaCl was used as the flux, it could not oxidize Ta, as the former does not contain oxygen. The surface of the Ta substrate dissolved slightly in NaCl, and a small amount of a compound corresponding to the Ta-Cl system was formed as the precursor material, because $TaCl_5$ was also nitrided to Ta_3N_5.[27] As a result, a few small Ta_3N_5 crystals were synthesized in the NH_3 flow.

Next, we compare the mechanisms by which Ta_3N_5 crystal layers were formed when $NaNO_3$ (Run No. 1) and Na_2CO_3 (Run No. 2, 4, 5) were used as the fluxes. When

$NaNO_3$ was used as the flux, the Ta_3N_5 crystals were formed by a process different from those when the other fluxes were used; this was owing to the fact that the melting point of $NaNO_3$ (308 °C) is relatively low. The process for the formation of Ta_3N_5 crystals using $NaNO_3$ as the flux is illustrated in Fig. S4a. $NaNO_3$ melted at approximately 300 °C during the temperature elevating process and reacted with Ta surface of the substrate. This resulted in the growth of polyhedral $NaTaO_3$ crystals, as has been mentioned previously.[28] At this temperature, NH_3 gas does not react with the Ta, because the decomposition temperature of NH_3 is 600 °C or higher.[29] Further, the reaction between $NaNO_3$ and the Ta surface is not affected by NH_3. $NaNO_3$ decomposes at approximately 360 °C to produce $NaNO_2$ and O_2; further heating mainly produces Na_2O. $NaNO_3$ is consumed by the formation of $NaTaO_3$ crystals via $NaNO_2$ and Na_2O. Almost all of the $NaNO_3$ is consumed at approximately 600 °C, which is the decomposition temperature of NH_3. Next, the $NaTaO_3$ is transformed into Ta_3N_5 by nitridation both before and during the holding process (holding temperature of 850 °C). The crystal-layer fabrication method employed in this study is a single-step process, that is, it only involves one heating stage, in which heating is performed in an NH_3 flow; however, the actual process for the formation of the Ta_3N_5 crystal layer is a two-step one, involving the fabrication of $NaTaO_3$ and its subsequent nitridation to Ta_3N_5. This process is almost the same as one reported previously;[17] the difference is that, in the present case, $NaTaO_3$ is produced in an NH_3 flow and not in an atmosphere rich in oxygen. The nitridation process resulted in numerous pores on the surfaces of the synthesized crystals, owing to the change in the crystal structure resulting from the change in the crystal phase. In addition, a dark red (*i.e.*, thick) layer of Ta_3N_5 crystals was formed, because a thick layer of $NaTaO_3$ crystals was grown owning to the use of a low heating rate (10 $°C \cdot min^{-1}$). This was in contrast to the previous study, in which the $NaTaO_3$ crystal layer was formed using a heating rate as high as 100 $°C \cdot min^{-1}$. As described above, the Ta_3N_5 crystal layer was formed in two steps, owing to the low melting point of $NaNO_3$. To obtain a layer consisting of Ta_3N_5 single crystals, both the formation of the precursor-oxide phases and their nitridation should occur simultaneously in the solution (*i.e.*, the liquid phase).

In contrast, Na_2CO_3 has a melting point of 851 °C; therefore, the precursor $NaTaO_3$ does not form readily before the decomposition of the NH_3 gas (*i.e.*, at temperatures lower than 600 °C). During the fabrication of the Ta_3N_5 crystal layer using Na_2CO_3 as the flux, Na_2CO_3 melted at approximately 850 °C during the holding process. Thus, both the formation of the precursor phases and their nitridation occurred almost simultaneously, as is the case when Ta_3N_5 crystals are grown from a solution.

The process for the formation of Ta_3N_5 crystals using Na_2CO_3 as the flux is illustrated in Fig. S4b. Well-developed Ta_3N_5 crystals surrounded by flat surfaces could be grown successfully, as shown in Fig. 1b.

However, the thus-formed crystal layer exhibited poor uniformity and coverage, as shown in Fig. S1b, because the holding temperature was the same as the melting point of Na_2CO_3. Therefore, the melt reacted with the surface of the Ta substrate before it could spread uniformly and wet the surface. This problem can be solved by using a higher holding temperature. However, in this case, the Ta substrate would get directly nitrided into other tantalum nitrides such as Ta_5N_6 and Ta_2N.[10] Therefore, the holding temperature was kept at 850 °C, and the flux used was one having a melting (or dissolution) temperature that lay between the decomposition temperature of NH_3 (*i.e.*, greater than 600 °C) and the holding temperature (850 °C). When NaCl and Na_2CO_3 are mixed in a molar ratio of 4:1, the liquidus temperature is approximately 730 °C.[30] That is to say, the melting point of Na_2CO_3 decreases from 851 °C to 730 °C. Consequently, when NaCl-Na_2CO_3 was used as the flux, it increased the uniformity and degree of coverage of the formed Ta_3N_5 crystal layer, as shown in Fig. S1d and S1e. It is assumed that this was because the flux spread uniformly on the surface of the Ta substrate, subsequently reacting with the surface and NH_3. In view of the crystal layers formed using Na_2CO_3 and NaCl individually as fluxes, the Ta surface was dissolved mainly by Na_2CO_3, with NaCl aiding the spreading of Na_2CO_3. When 10 μL of NaCl-Na_2CO_3 (Run No. 4) and Na_2CO_3 alone (Run No. 2) were used as the fluxes, the amount of Na_2CO_3 coated on the surface of the Ta substrate was greater than that when 5 μL of NaCl-Na_2CO_3 was used as the flux. The crystal layers fabricated using these fluxes exhibited XRD patterns that contained weak diffraction lines corresponding to $NaTaO_3$. This was either because a large amount of $NaTaO_3$ was formed or because the nitridation process was blocked by Na_2CO_3, which was redundant.

Table S1 shows the crystallite sizes obtained from the XRD patterns of the crystal layers. The crystals fabricated using NaCl and NaCl-Na_2CO_3 as the fluxes had larger crystallite sizes than those of the crystals fabricated using $NaNO_3$ and Na_2CO_3. We believe that the evaporation of the flux was the driving force for the growth of the Ta_3N_5 crystals. NaCl evaporates readily compared to the other fluxes. Therefore, highly crystalline Ta_3N_5 was fabricated when the NaCl was employed as the flux.

Process for formation of Ta_3N_5 crystal layer using NaCl-Na_2CO_3 as flux

Next, crystal layers were fabricated at various holding temperatures using NaCl-Na_2CO_3 as the flux (molar ratio = 4:1, amount of flux used = 5 μL). The holding time was fixed to 0 h (*i.e.*, the samples were heated to the highest temperature and then cooled immediately), keeping in mind the formation process of the Ta_3N_5 crystal layers. For convenience, we have used the terms "holding temperature" and “holding time” even when the holding time was zero. Fig. S5 shows digital photographs of the crystal layers fabricated at various temperatures. The crystal layers fabricated at temperatures lower than 800 °C were almost white. On the other hand, a red crystal layer was obtained at 850 °C (Fig. S5d). SEM images showed that the crystal layer prepared at 700 °C had a lower surface roughness than those of the other layers (Fig. 3a). In the former case, the flux could not dissolve the surface of the Ta substrate to a sufficient degree, owing to the low temperature and the short heating time. At 750 °C, small prismatic and cuboid crystals were observed. The surface roughness increased, because the heating temperature exceeded the liquidus temperature of the NaCl-Na_2CO_3, resulting in the rapid dissolution of the surface of the Ta substrate. In the case of the crystal layer fabricated at 800 °C, the number of prismatic crystals formed was higher. At 850 °C, almost all the crystals formed were prismatic. Further, they were larger than those formed at temperatures lower than 800 °C. The prismatic and cuboid crystals are presumed to be of Ta_3N_5 and $NaTaO_3$, respectively. When nitrogen is incorporated during the fabrication process, prismatic Ta_3N_5 crystals are generated. In contrast, using a poor nitrogen source resulted in cuboid $NaTaO_3$. Fig. 4 shows the XRD profiles for the crystal layers fabricated at 700−850 °C for 0 h. At 700 °C, no diffraction line corresponding to Ta_3N_5 was observed (Fig. 4a). On increasing the heating temperature, the intensity of the diffraction lines corresponding to $NaTaO_3$ and Ta_3N_5 decreased and increased, respectively. At 850 °C for 0 h, Ta_3N_5 became the main phase (Fig. 4d). Finally, the crystal layer fabricated at a holding temperature of 850 °C and a holding time of 1 h did not exhibit a diffraction line corresponding to $NaTaO_3$, as shown in Fig. 2e.

Next, on the basis of the SEM and XRD results, we discuss the formation of crystal layers when NaCl-Na_2CO_3 is used as the flux. In the case of the layer fabricated at 700 °C, assuming that the decomposition temperature of NH_3 gas is approximately 600 °C, the flux-coated Ta substrate is heated for only approximately 11 min in an atmosphere of decomposed NH_3, given that the heating rate is 10 $°C\cdot min^{-1}$. The NaCl-Na_2CO_3 flux dissolves the surface of the Ta substrate slightly and reacts with it. As a result, cuboid $NaTaO_3$ crystals grow without there being a reaction with NH_3. By increasing the holding temperature and holding time, nitrogen can be incorporated into the crystals in a large enough concentration during crystallization. Therefore, Ta_3N_5 and $NaTaO_3$ are formed in greater and lower amounts, respectively. We believe that the prismatic Ta_3N_5 crystallized owing to flux evaporation.

PEC properties of the Ta_3N_5 crystal layers

Fig. S6 shows the absorption spectrum for the Ta_3N_5 crystal layer fabricated using NaCl-Na_2CO_3 as the flux at 850 °C for 1 h (see Supporting Information for experimental details). The optical absorption edge of the Ta_3N_5 crystals was approximately 600 nm, and their band gap was determined to be approximately 2.1 eV. Fig. 5 shows the current−potential curve for a Ta_3N_5 crystal layer modified with Co-Pi as a cocatalyst. The Ta_3N_5 crystal layer was formed using NaCl-Na_2CO_3 as the flux at 850 °C for 1 h. An anodic photocurrent associated with the oxidation of water was generated. The onset potential was measured to be approximately 0.4 V_{RHE}, while the photocurrent density was 1.5 $mA \cdot cm^{-2}$ at 1.23 V_{RHE}. That the performance of this modified layer was relatively quite poor might be attributed to its low thickness, impurities, and the state of the substrate/crystal layer interface. However, these results indicated that Ta_3N_5 crystal layers fabricated using the proposed flux coating method can potentially be used as n-type semiconductor electrodes under visible-light irradiation.

Conclusion

Layers of Ta_3N_5 crystals were fabricated by a novel flux coating method in an NH_3 flow. The thus-synthesized crystal layers exhibited good adhesion to the substrate, because the Ta component of Ta_3N_5 was provided by the Ta substrate, and the Ta_3N_5 crystals grew directly on the substrate. The shape of the individual crystals constituting the crystal layer was determined by the flux used. The crystal layer fabricated using NaCl-Na_2CO_3 as the flux consisted of well-formed, prismatic crystals surrounded by flat surfaces, while that formed using $NaNO_3$ as the flux consisted of cuboid crystals whose surfaces were covered with numerous pores. Thus, to synthesize a layer of well-formed Ta_3N_5 crystals, compounds having the appropriate melting point and a high ability to dissolve Ta should be used as the flux. That is to say, the flux should exhibit high solubility and reactivity with respect to Ta. However, the flux and its components should not remain in the crystal layer because the sodium compounds used as the flux are “extra” components as far as the Ta_3N_5 phase is concerned. In addition, a Ta_3N_5 crystal layer modified with Co-Pi as a cocatalyst acted as a photoelectrode under visible-light irradiation; this was confirmed by PEC measurements. Finally, we believe that the proposed method of fabricating crystal layers using a flux coating in an NH_3 flow could be used to fabricate crystal layers of several other nitrides as well.

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Figure captions

Table 1 Conditions for the synthesis of Ta_3N_5 crystal layers.

Fig. 1 Surface SEM images of the crystal layers fabricated using (a) $NaNO_3$ (Run No. 1), (b) Na_2CO_3 (Run No. 2), (c) NaCl (Run No. 3), and (d−f) NaCl-Na_2CO_3 as the fluxes. (d) 10 μL (Run No. 4) and (e, f) 5 μL (Run No. 5) of an aqueous NaCl-Na_2CO_3 solution were used as the fluxes.

Fig. 2 XRD profiles of the crystal layers fabricated using (a) $NaNO_3$ (Run No. 1), (b) Na_2CO_3 (Run No. 2), (c) NaCl (Run No. 3), and (d, e) NaCl-Na_2CO_3 as the fluxes; ICDD PDFs of (f) $NaTaO_3$ and (g) Ta_3N_5. (d) 10 μL (Run No. 4) and (e) 5 μL (Run No. 5) of an aqueous NaCl-Na_2CO_3 solution were used as the fluxes.

Fig. 3 SEM images of the crystal layers fabricated using NaCl-Na_2CO_3 as the flux at different holding temperatures and a holding time of 0 h: (a) 700 °C (Run No. 6), (b) 750 °C (Run No. 7), (c) 800 °C (Run No. 8), and (d) 850 °C (Run No. 9).

Fig. 4 XRD profiles of the crystal layers fabricated using NaCl-Na_2CO_3 as the flux at different holding temperatures and a holding time of 0 h: (a) 700 °C (Run No.

6), (b) 750 °C (Run No. 7), (c) 800 °C (Run No. 8), and (d) 850 °C (Run No. 9). ICDD PDFs of (e) $NaTaO_3$ and (f) Ta_3N_5.

Fig. 5 Current-potential curves for Co-Pi/Ta_3N_5/Ta. The Ta_3N_5 crystal layer was fabricated using NaCl-Na_2CO_3 as the flux at 850 °C for 1 h (Run No. 5). The electrolyte was a 0.2 M aqueous Na_2SO_4 solution with a pH of 13, which was adjusted by adding NaOH. The photoelectrode was irradiated with a 300 W Xe lamp equipped with a cut-off filter (λ > 420 nm). The electrode potential was swept in the positive direction at a rate of 10 $mV \cdot s^{-1}$.

Table S1 Crystallite sizes of the crystal layers fabricated using the various fluxes.

Fig. S1 Digital photographs of the crystal layers fabricated using (a) $NaNO_3$ (Run No. 1), (b) Na_2CO_3 (Run No. 2), (c) NaCl (Run No. 3), and (d, e) NaCl-Na_2CO_3 as the fluxes. (d) 10 μL (Run No. 4) and (e) 5 μL (Run No. 5) of an aqueous NaCl-Na_2CO_3 solution were used as the fluxes.

Fig. S2 Low-magnification surface SEM images of the crystal layers fabricated using (a) $NaNO_3$ (Run No. 1), (b) Na_2CO_3 (Run No. 2), (c) NaCl (Run No. 3), and (d,

e) NaCl-Na_2CO_3 as the fluxes. (d) 10 μL (Run No. 4) and (e) 5 μL (Run No. 5) of an aqueous NaCl-Na_2CO_3 solution were used as the fluxes.

Fig. S3 Cross-sectional SEM image of the crystal layer fabricated using NaCl-Na_2CO_3 as the flux at 850 °C for 1 h (Run No. 5).

Fig. S4 Illustration of the formation mechanism of Ta_3N_5 crystal layers using (a) $NaNO_3$, (b) Na_2CO_3, and (c) NaCl-Na_2CO_3 as the fluxes.

Fig. S5 Digital photographs of the crystal layers fabricated using NaCl-Na_2CO_3 as the flux at different holding temperatures and a holding time of 0 h: (a) 700 °C (Run No. 6), (b) 750 °C (Run No. 7), (c) 800 °C (Run No. 8), and (d) 850 °C (Run No. 9).

Fig. S6 UV-vis absorption spectrum of the crystal layers fabricated on the silica-glass substrate using NaCl-Na_2CO_3 as the flux at 850 °C for 1 h.

Table 1 Conditions for the synthesis of Ta_3N_5 crystal layers.

run no.	flux (molar ratio)	flux $NaNO_3$ / g	 Na_2CO_3 / g	 NaCl / g	water /mL	Na conc. / M	holding temp. / °C	holding time / h
1	$NaNO_3$	1.700	-	-	10	2	850	1
2	Na_2CO_3	-	1.060	-	10	2	850	1
3	NaCl	-	-	1.169	10	2	850	1
4	NaCl-Na_2CO_3 (4:1)	-	0.424	0.935	10	2.4	850	1
5	NaCl-Na_2CO_3 (4:1)	-	0.424	0.935	10	2.4	850	1
6	NaCl-Na_2CO_3 (4:1)	-	0.424	0.935	10	2.4	700	0
7	NaCl-Na_2CO_3 (4:1)	-	0.424	0.935	10	2.4	750	0
8	NaCl-Na_2CO_3 (4:1)	-	0.424	0.935	10	2.4	800	0
9	NaCl-Na_2CO_3 (4:1)	-	0.424	0.935	10	2.4	850	0

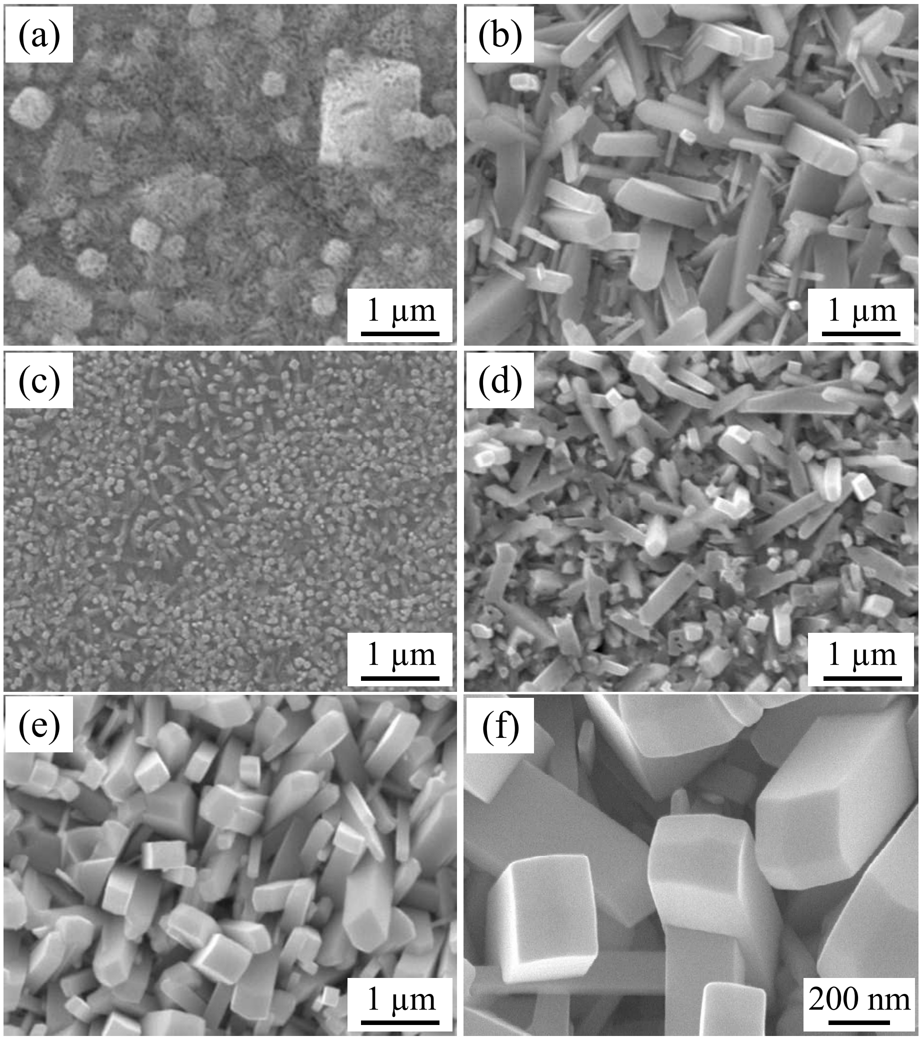


Fig. 1 Surface SEM images of the crystal layers fabricated using (a) $NaNO_3$ (Run No. 1), (b) Na_2CO_3 (Run No. 2), (c) NaCl (Run No. 3), and (d−f) NaCl-Na_2CO_3 as the fluxes. (d) 10 µL (Run No. 4) and (e, f) 5 µL (Run No. 5) of an aqueous NaCl-Na_2CO_3 solution were used as the fluxes.

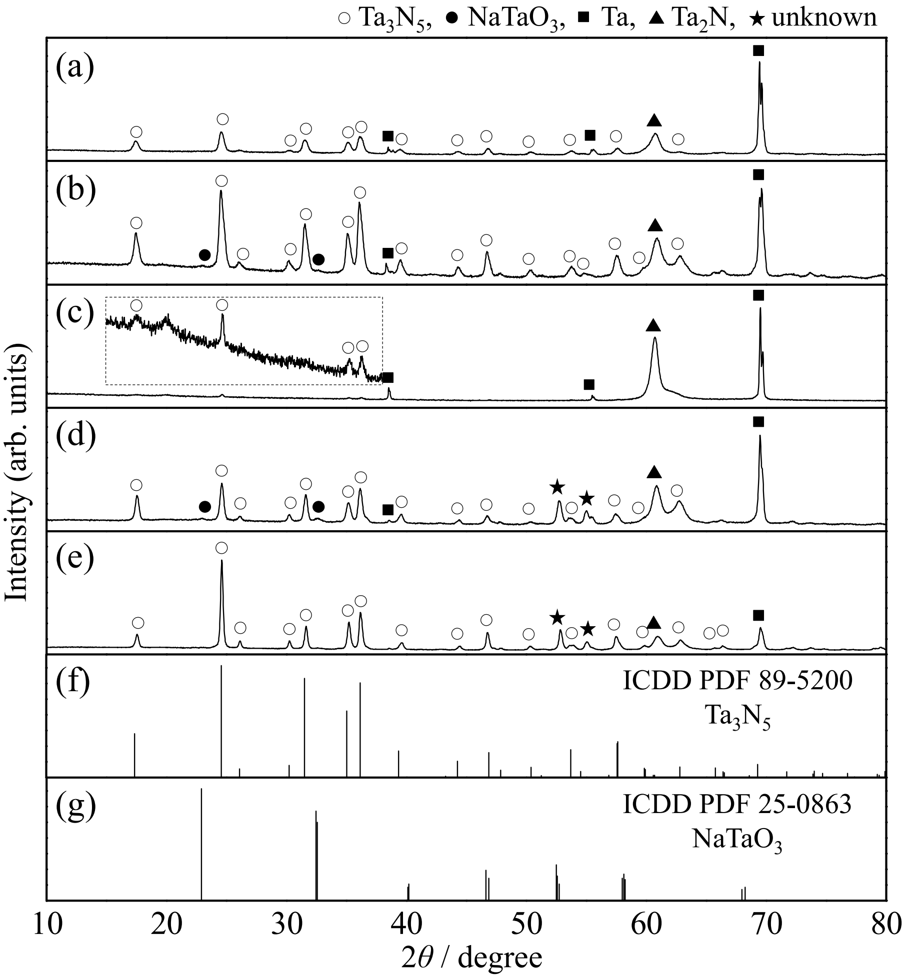


Fig. 2 XRD profiles of the crystal layers fabricated using (a) $NaNO_3$ (Run No. 1), (b) Na_2CO_3 (Run No. 2), (c) NaCl (Run No. 3), and (d, e) NaCl-Na_2CO_3 as the fluxes; ICDD PDFs of (f) $NaTaO_3$ and (g) Ta_3N_5. (d) 10 μL (Run No. 4) and (e) 5 μL (Run No. 5) of an aqueous NaCl-Na_2CO_3 solution were used as the fluxes.

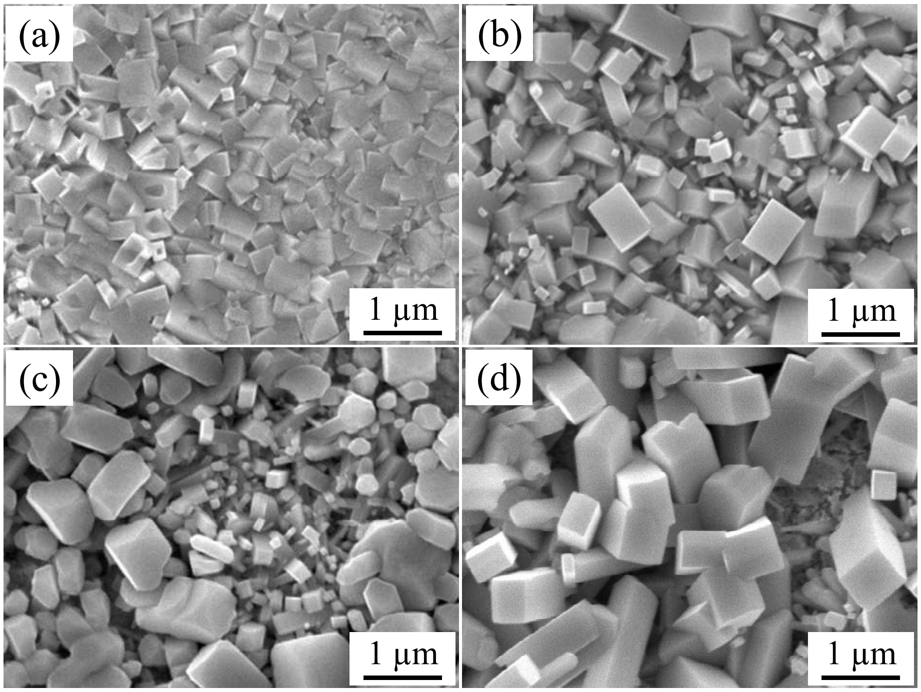
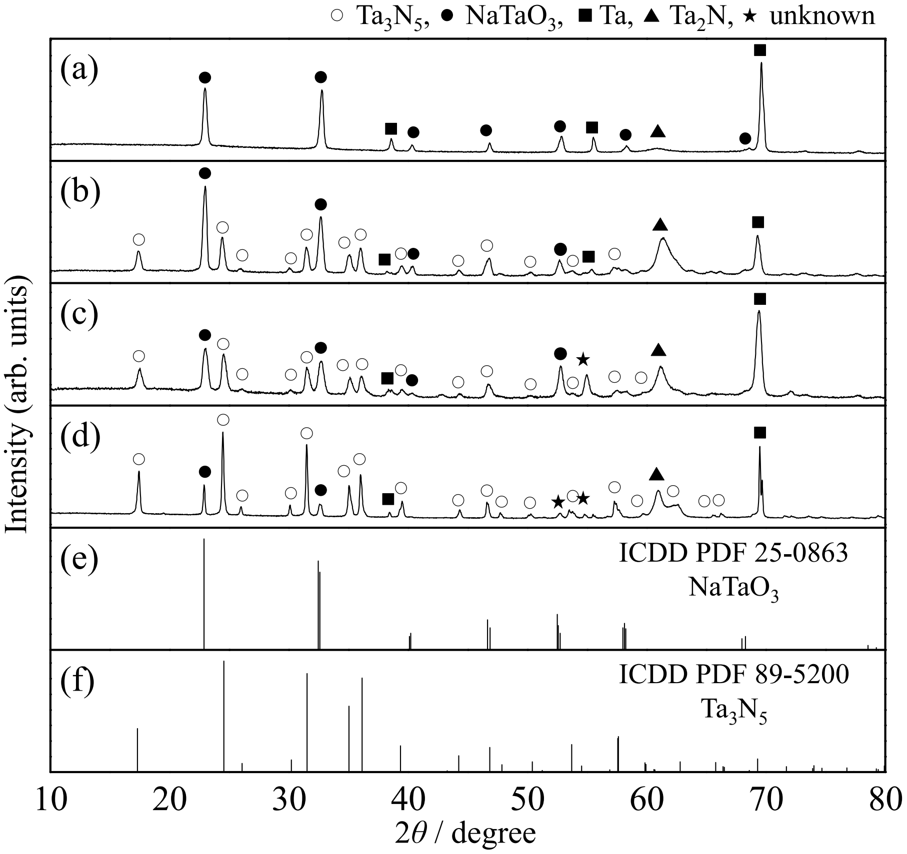


Fig. 3 SEM images of the crystal layers fabricated using NaCl-Na_2CO_3 as the flux at different holding temperatures and a holding time of 0 h: (a) 700 °C (Run No. 6), (b) 750 °C (Run No. 7), (c) 800 °C (Run No. 8), and (d) 850 °C (Run No. 9).



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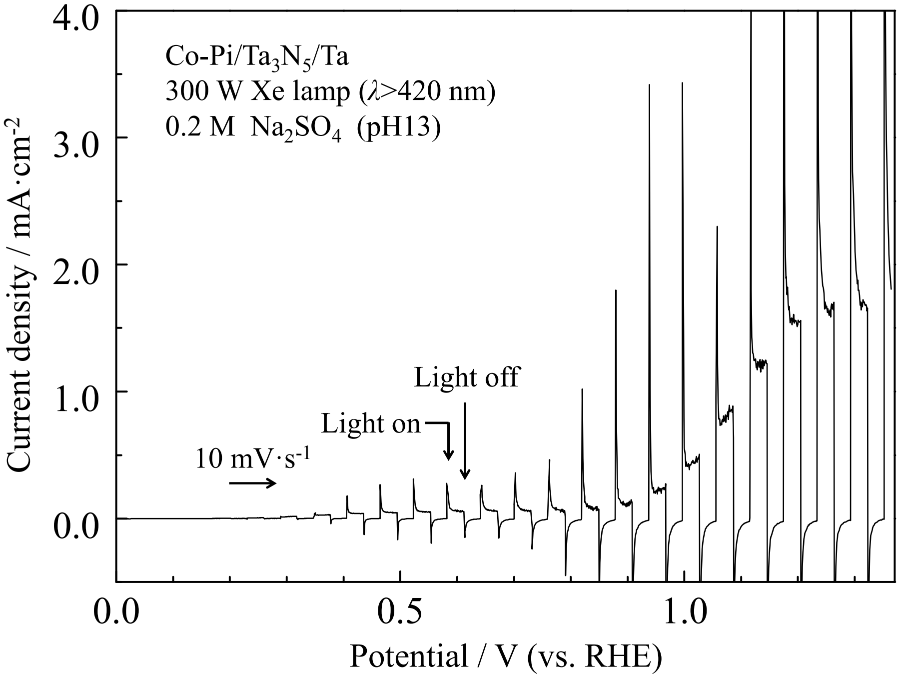

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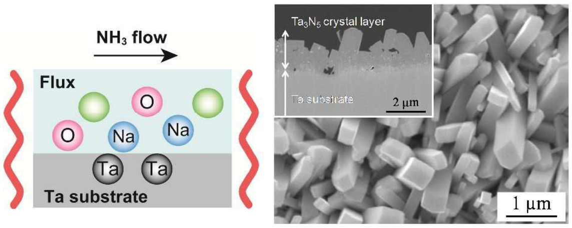
A graphical abstract



Ta_3N_5 crystal layers were fabricated on Ta substrates by a novel flux coating method in an NH_3 flow.