Electronic Supplementary Information (ESI)

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

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Materials and reagents

To fabricate the Ta_3N_5 crystal layers, Ta foil (99.95 %, Nilaco Corporation), $NaNO_3$ (99.0 %, Wako Pure Industries, Ltd.), NaCl (99.5 %, Wako Pure Industries, Ltd.), and Na_2CO_3 (99.8 %, Wako Pure Industries, Ltd.) were used. The solution-coated substrates were heated using NH_3 (99.9995 %, Sumitomo Seika Chemicals Co., Ltd.) and N_2 (99.9995 %, Taiyo Nippon Sanso Corporation) gases. For the modification using a cocatalyst, $Co(NO_3)_2 \cdot 6H_2O$ (99.5 %, Wako Pure Industries, Ltd.), K_2HPO_4 (99.0 %, Kanto Chemicals), KH_2PO_4 (99.5 %, Kanto Chemicals), Na_2SO_4 (99.0 %, Wako Pure Industries, Ltd.), and NaOH (97.0 %, Wako Pure Industries, Ltd.) were used. All the chemicals were used as-purchased without further purification.

Fabrication of samples for UV-vis spectral measurements

We could not measure the Kubelka-Munk spectrum for the Ta_3N_5 crystal layers on the Ta substrate with accuracy, because of absorption by the Ta substrate. Therefore, we fabricated the Ta_3N_5 crystal layers on a silica-glass substrate, and subsequently measured their light absorption properties in the transmission mode.

First, a layer of Ta was deposited on the silica-glass substrate (20 × 20 × 0.5 mm) by sputtering (Kenix Co., Ltd., RF sputter system, KXS-410B) using a Ta target (99.99 %, High Purity Chemicals). The deposited Ta layer had a thickness of approximately 60 nm. The subsequent procedures for the fabrication of the Ta_3N_5 crystal layers were basically the same as those of the fabrication of the layers on the Ta substrates. The Ta layer was dry-cleaned and hydrophilized by being irradiated under vacuum-ultraviolet light (λ = 172 nm). Next, 13.3 μL of the NaCl-Na_2CO_3 aqueous solution was placed on the Ta layer. Because 5 μL of the solution was used for the Ta substrates, which had dimensions of 10 × 15 mm, the amount of solution used was increased to 13.3 μL for the silica-glass substrates, which were larger in size (dimensions of 20 × 20 mm). The solution-coated substrates were dried in an electric oven at 100 °C for 30 min. Subsequently, the substrates were heated to 850 °C at a rate of 10 °C·min^{-1} and held at this temperature for 1 h in an NH_3 flow (100 mL·min^{-1}).

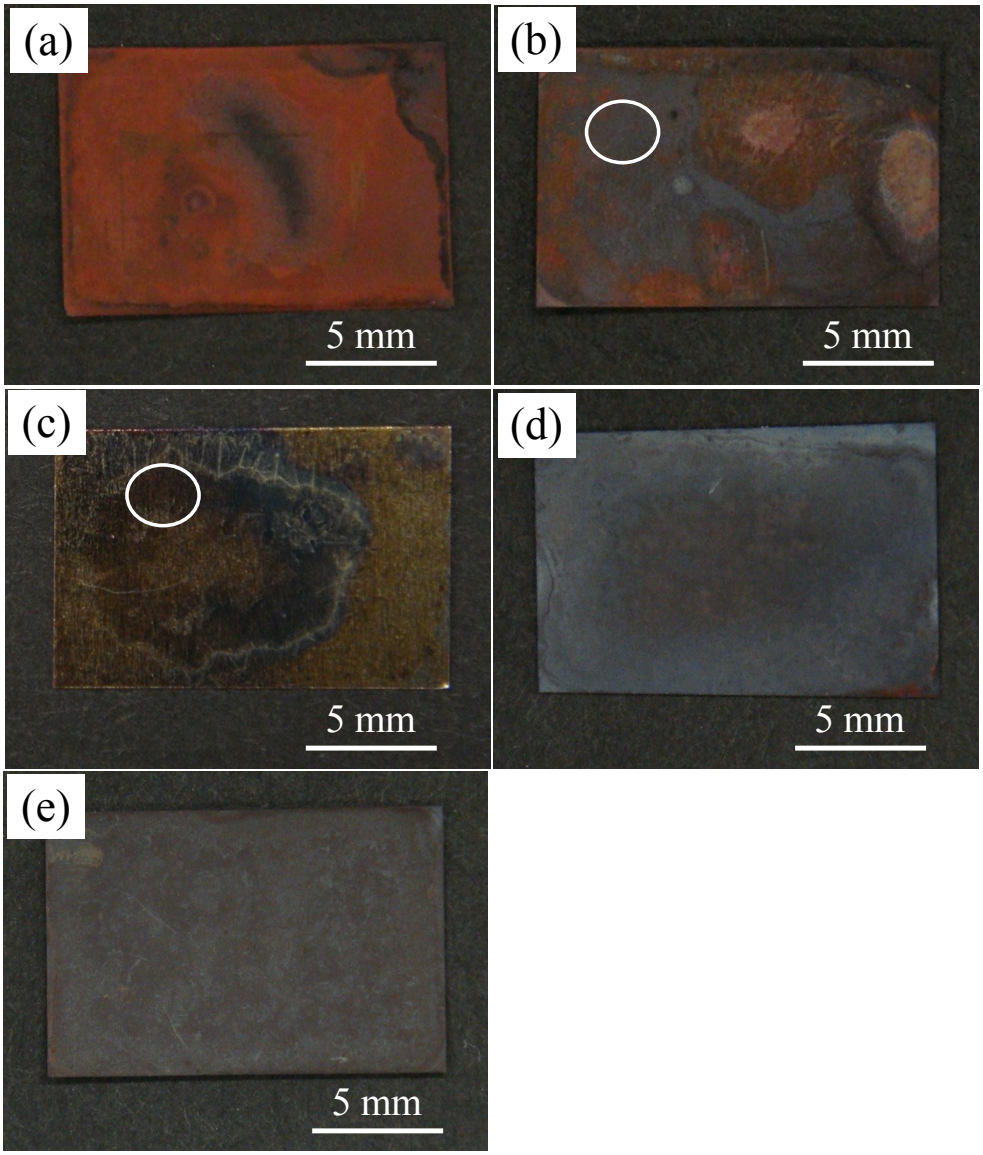

Fig. S1 Digital photographs of the crystal layers fabricated using (a) $NaNO_3$ (Run No. 1), (b) Na_2CO_3 (Run No. 2), (c) NaCl (Run No. 3), and (d, e) NaCl-Na_2CO_3 as the fluxes. (d) 10 μL (Run No. 4) and (e) 5 μL (Run No. 5) of an aqueous NaCl-Na_2CO_3 solution were used as the fluxes.

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

run no.	flux (molar ratio)	amount of coating / μL	crystallite size / nm
1	$NaNO_3$	10	18.3
2	Na_2CO_3	10	18.0
3	NaCl	10	36.6
4	NaCl-Na_2CO_3 (4 : 1)	10	31.1
5	NaCl-Na_2CO_3 (4 : 1)	5	36.1

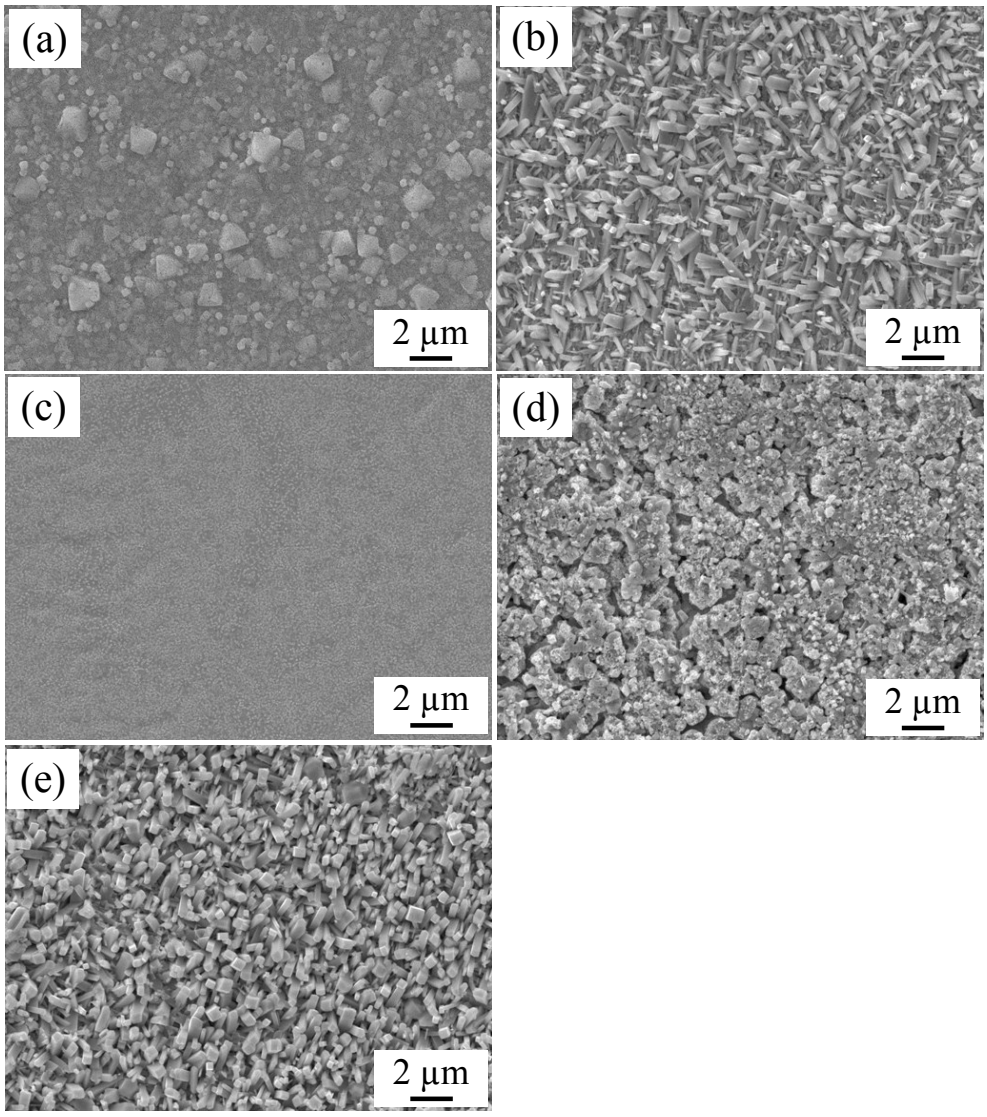

Fig. S2 Low-magnification surface SEM images of the crystal layers fabricated using (a) $NaNO_3$ (Run No. 1), (b) Na_2CO_3 (Run No. 2), (c) NaCl (Run No. 3), and (d, e) NaCl-Na_2CO_3 as the fluxes. (d) 10 μL (Run No. 4) and (e) 5 μL (Run No. 5) of an aqueous NaCl-Na_2CO_3 solution were used as the fluxes.

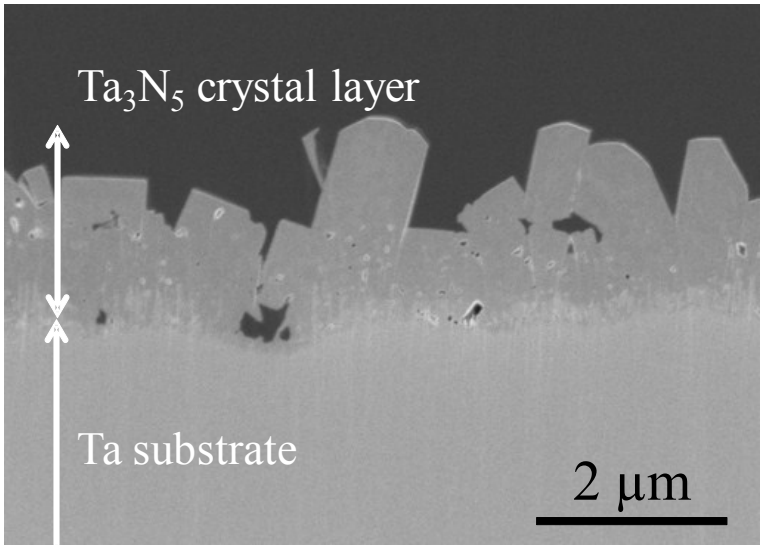

Fig. S3 Cross-sectional SEM image of the crystal layer fabricated using NaCl-Na_2CO_3 as the flux at 850 °C for 1 h (Run No. 5).

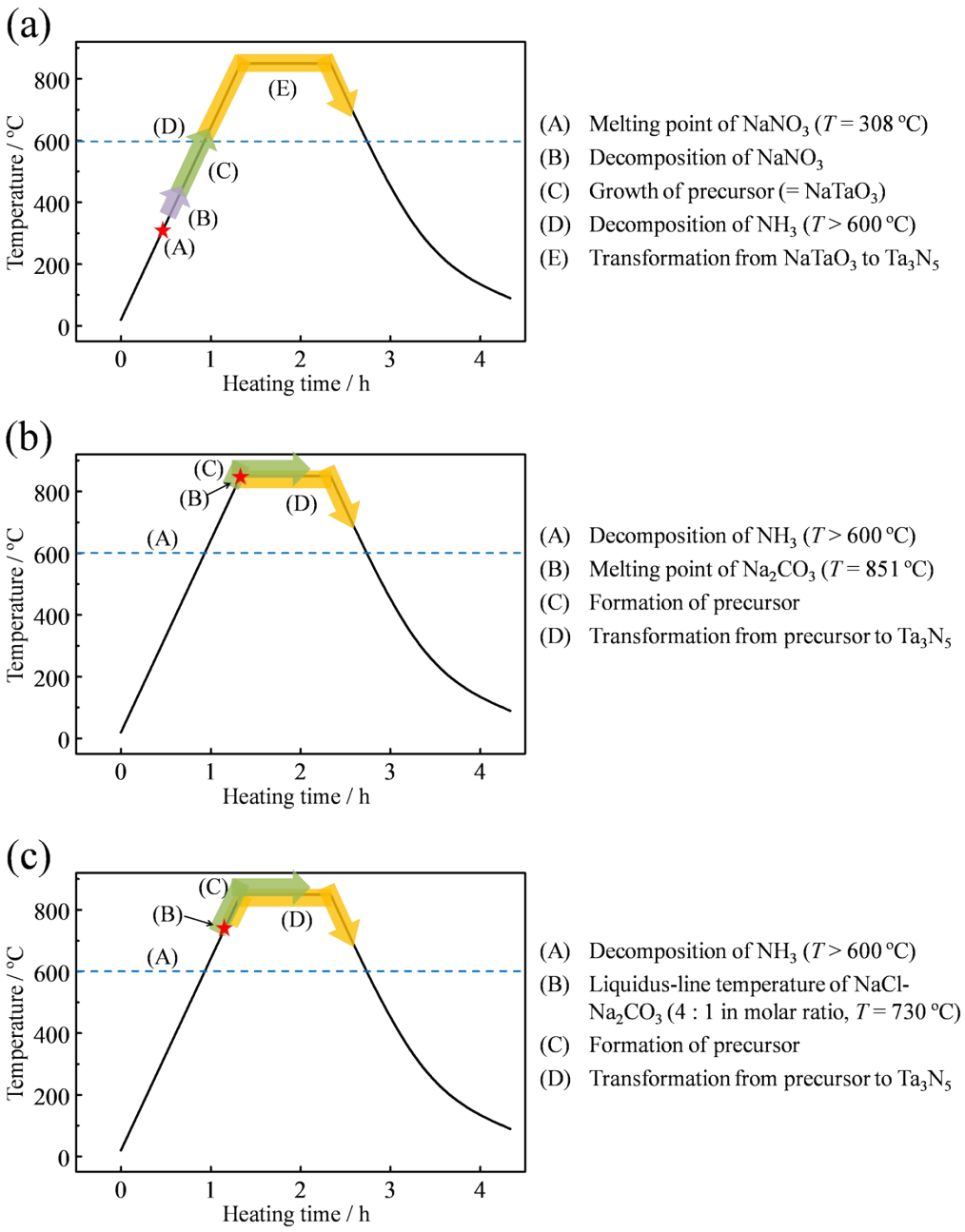

Fig. S4 Illustration of the formation mechanism of Ta_3N_5 crystal layers using (a) $NaNO_3$, (b) Na_2CO_3, and (c) NaCl-Na_2CO_3 as the fluxes.

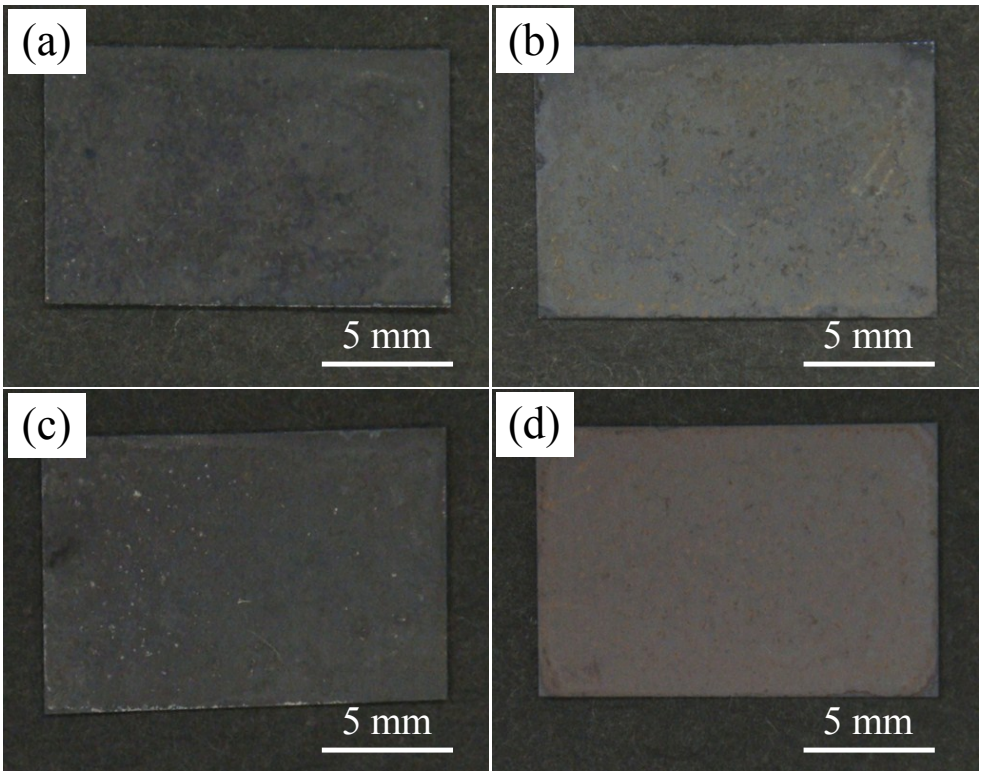

Fig. S5 Digital photographs of the crystal layers fabricated using NaCl-Na_2CO_3 as the flux at different holding temperatures and a holding time of 0 h: (a) 700 °C (Run No. 6), (b) 750 °C (Run No. 7), (c) 800 °C (Run No. 8), and (d) 850 °C (Run No. 9).

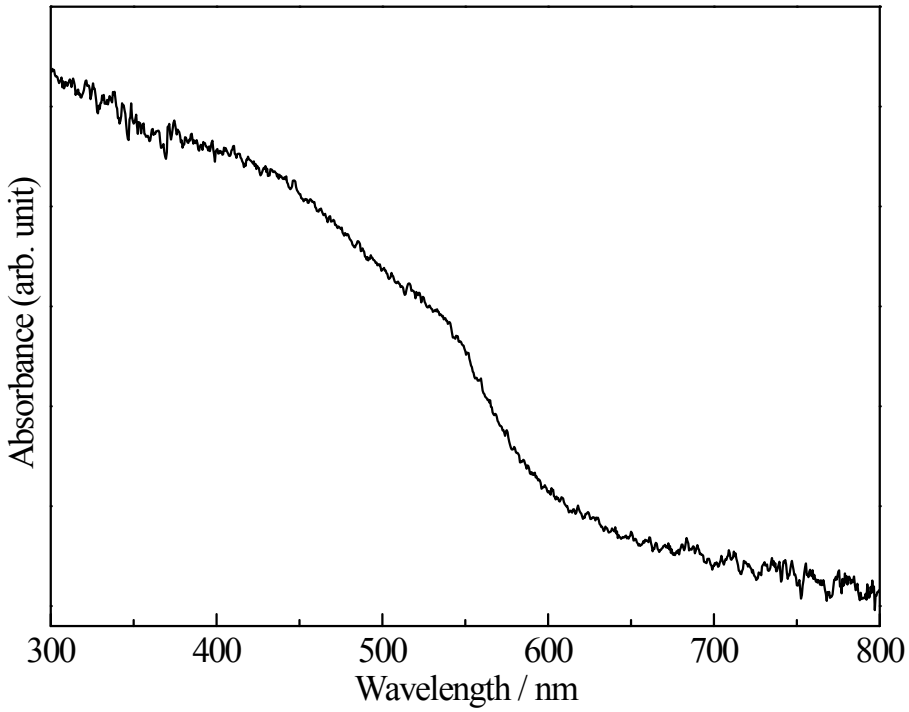

Fig. S6 UV-vis absorption spectrum of the crystal layers fabricated on the silica-glass substrate using NaCl-Na_2CO_3 as the flux at 850 °C for 1 h.