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Solution-processed oxide semiconductor SnO in p-channel thin-film transistors

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Experimental details

Powder synthesis

In a typical powder synthesis, 250 mg of tin(II) chloride dihydrate ($SnCl_2$•$2H_2O$; 99.995 %; Alfa Aesar) was ground using an agate mortar and pestle, was added in a 10 mL vial with 1 mL of ammonium hydroxide (NH_4OH; 28-30 %; Sigma-Aldrich), was filtered through a binder-free glass fiber membrane (GF/C; Whatman), was washed with an additional 5 mL of NH_4OH, and was intensively washed with deionized water to remove NH_4OH and the by-product NH_4Cl that is highly soluble in water. The filtered substance was then transferred to be on a combustion boat and was introduced into a fused silica tube. The tube was purged for 3 h at a flow rate of 0.2 L min^{-1} with purified forming gas, which was composed of N_2 and H_2 at a volume ratio of 92 and 8 % and was thoroughly purified through H_2O and O_2 traps (GMT, OT1, and IOT; Agilent) to a nominal H_2O and O_2 concentration of 6 ppb and 2 ppb, respectively. The annealing temperature was then increased from room temperature to an indicated temperature of 200-600 °C at a rate of 10 °C min^{-1} with the forming gas flowed at a rate of 0.1 L min^{-1}, was kept at the temperature for 2 h, and was left to be cooled down to room temperature. The resultant substance was ground using the mortar and pestle before X-ray diffraction (XRD) measurements.

Substrate cleaning

Si substrates and glass substrates were immersed and cleaned in a mixture of sulfuric acid (H_2SO_4; 95-97%; Merck) and hydrogen peroxide (H_2O_2; 30%; Merck) at a volume ratio of 4:1 for 10 min, followed by a thorough rinse with deionized water. The procedure was repeated twice to confirm the cleanliness and to minimize an experimental error.

Thin-film synthesis for XRD measurements

In a thin-film synthesis for XRD measurements, 113 mg of $SnCl_2$•$2H_2O$ was dissolved in a 10 mL vial with 1 mL of anhydrous methanol (99.8 %; Sigma-Aldrich) at a concentration of 0.5 M in a N_2-filled glove box that had both H_2O and O_2 concentrations less than 1 ppm. The solution was stirred with a magnetic stirrer for 1 h and was spin-coated on a glass substrate at a speed of 2000 rpm for 30 sec in the glove box. The substrate was kept in a sealed box filled with the same N_2 without exposure to air, was transferred to a glove bag that had been purged with N_2 generated from liquid N_2, and was exposed to the vapor of NH_4OH for 1 h. The substrate was taken out of the glove bag and was rinsed with deionized water to remove NH_4OH and NH_4Cl. The substrate was then transferred to be on a combustion boat and was introduced into a fused silica tube. The tube was purged with the purified forming gas for 1 h at a flow rate of 0.2 L min^{-1}. The annealing temperature was then increased from room temperature to an indicated temperature of 200-600 °C at a rate of 10 °C min^{-1} with the forming gas flowed at a rate of 0.1 L min^{-1}, was kept at the temperature for 2 h, and was left to be cooled down to room temperature.

Thin-film synthesis for transistors

In a typical thin-film synthesis for transistors, 23 mg of $SnCl_2{\bullet}2H_2O$ was dissolved in a 10 mL vial with 1 mL of the methanol at a concentration of 0.1 M in the N_2-filled glove box. The solution was stirred with a magnetic stirrer for 1 h and was spin-coated in the glove box at a speed of 3000 rpm for 30 sec on a lightly doped p-type Si(100) substrate, which had a resistivity of 2.75 Ω cm, with a thermally grown SiO_2 dielectric of 200 nm thickness. The substrate was then processed in the same manner as in the thin-film synthesis for XRD measurements.

Thin-film morphology and thickness observation

Surface morphologies of the thin films were observed both by a scanning electron microscope (SEM), LEO 1530 (Carl Zeiss SEM), and by an atomic force microscope (AFM), NanoScope III (Veeco), in the tapping-mode employing cantilevers, NSC15/No Al (MIKROMASCH). Thin film thickness was measured using the AFM.

XRD measurements for powder and thin film

XRD measurements were preformed using an XRD system, X'Pert-MRD (PANalytical), equipped with a Cu anode tube that was operated at a tube current and voltage of 40 mA and 45 kV, respectively, in the Bragg-Brentano geometry. Measurement parameters were chosen to be a 2θ step size of 0.02 °, measurement duration of 200 sec per step, irradiation length and width of 5 mm and 4 mm, respectively. Four independent measurements were averaged to increase the signal-to-noise ratio.

XRD measurements for Si(100) reference

A heavily doped n-type Si(100) substrate, which had a resistivity smaller than 0.01 Ω cm, was employed as a reference to determine the degree of instrumental broadening. The same measurement parameters, as chosen for the powder and thin film, were also used for the Si(100) reference except a measurement duration of 10 sec per step.

XRD plots calculated on the basis of a reference pattern

The reference patterns, $Sn_6O_4(OH)_4$ (International Center for Diffraction Data - Powder Diffraction File (ICDD-PDF): 01-084-2157), SnO (01-072-1012), SnO_2 (00-041-1445), and Sn (00-004-0673), were employed. A set of diffraction pattern that corresponds to Cu-$K_{\alpha 1}$ line (the wavelength $\lambda_{\text{Cu-}K\alpha 1}$ of 1.54060 Å) was calculated on the basis of a reference pattern, and a XRD plot was simulated by convoluting the set of diffraction pattern with Lorentzians which had a full-width at half maximum (FWHM) of 0.1 °. Another XRD plot that corresponds to Cu-$K_{\alpha 2}$ line ($\lambda_{\text{Cu-}K\alpha 2}$ of 1.54443 Å) was also simulated in the same manner as in Cu-$K_{\alpha 1}$ line. The two XRD plots were then superimposed at an integrated intensity ratio $A_{\text{Cu-}K\alpha 1}/A_{\text{Cu-}K\alpha 2}$ of 1.82, which is determined from the (400) diffraction of a Si(100) substrate, as listed in Table S1.

Thin-film transistor (TFT) measurements

Current-voltage (*I*-*V*) characteristics of tin monoxide (SnO) TFTs were measured using a semiconductor parameter analyzer, Agilent 4156C, at room temperature in a N_2-filled glove box, which had both H_2O and O_2 concentrations less than 1 ppm. The field-effect mobility μ_{FE} was extracted from the transfer characteristics in the saturation regime, according to the equation:[1]

$$\mu_{FE} = -\left(\frac{2}{C_i}\right)\left(\frac{L}{W}\right)\frac{I_{ds}}{\left(V_{gs} - V_{th}\right)^2}, \tag{S1}$$

where C_{i} is the gate capacitance per unit area, W and L are the channel width and length, respectively, and I_{ds}, V_{gs}, and V_{th} are the drain current, gate voltage, and threshold voltage, respectively. The on/off drain current ratio was defined in the transfer characteristics by the maximum current and off current measured at V_{gs} of -80 and 0 V, respectively.

XRD analyses in terms of crystallite size determination

Determination of instrumental parameters based on (400) diffraction from a Si(100) substrate

Fig. S1(a) shows the XRD plot of a heavily doped n-type Si(100) substrate. A strong and sharp doublet peak at an angle 2θ of 69.1 ° comes from the (400) diffraction but consists of two independent peaks, which correspond to Cu-$K_{\alpha1}$ line and Cu-$K_{\alpha2}$ line for 2θ of 69.14 and 69.34 °, respectively. The doublet peak is qualitatively modeled by two Lorentzian fittings, as seen in Fig. S1(b). The fitting parameters are summarized in Table S1, revealing that the X-ray source consists of Cu-$K_{\alpha1}$ line and Cu-$K_{\alpha2}$ line, which are well modeled by a Lorentzian that has a FWHM w of 0.0546 and 0.0568 °, respectively, and are superimposed at an integrated intensity ratio $A_{\text{Cu-}K\alpha1}/A_{\text{Cu-}K\alpha2}$ of 1.82.

It should also be worth mentioning in Fig. S1(a) that (1) a weak singlet peak at 2θ of 61.69 ° originates from the (400) diffraction of Cu-K_{β} line ($\lambda_{\text{Cu-}K\beta}$ of 1.39225 Å); (2) an abrupt decrease in intensity at and lower than 2θ of 66.5 ° corresponds to a Ni filter that has an X-ray absorption edge located between Cu-$K_{\alpha1,2}$ lines and Cu-K_{β} line, resulting in a significant attenuation of Cu-K_{β} line; (3) since the integrated intensity of Cu-K_{β} line is 0.0028 times smaller than that of Cu-$K_{\alpha1}$ line, in most powder XRD measurements, Cu-K_{β} diffractions are comparable with a background level and negligible; (4) a weak and sharp doublet peak at 2θ of 32.9 ° comes from the (200) diffraction but consists of two independent peaks, which correspond to Cu-$K_{\alpha1}$ line and Cu-$K_{\alpha2}$ line for 2θ of 32.97 and 33.05 °, respectively; and (5) the (200) diffraction should not be observed according to the selection rule for a diamond face-centered cubic structure of Si, but is actually observed as a weak doublet peak because the periodicity and symmetry break on the Si surface.

Crystallite size estimate according to Scherrer’s formula

Under the assumptions where (1) the crystallites do not have any significant strains since the tin oxide powder is synthesized under the thermal equilibrium condition; (2) the crystallite is spherical; and (3) an XRD peak is qualitatively modeled by a Lorentzian fitting, the crystallite diameter d_{cryst} is estimated on the basis of Scherrer’s formula:[S2]

$$d_{cryst} = \frac{0.9\lambda}{w_{cryst}\cos\theta_c}, \tag{S2}$$

where λ is the wavelength of X-ray that corresponds to the XRD peak, w_{cryst} is a FWHM of the Lorentzian fitting L_{cryst} that solely attributes to the crystallite size with the instrumental broadening excluded, and θ_{c} is the XRD peak position. Since the convolution of two given Lorentzians L_1 and L_2 that have a FWHM of w_1 and w_2, respectively, is mathematically described as

$$L_3(w_3) = L_1(w_1) \otimes L_2(w_2), \tag{S3}$$

$$w_3 = w_1 + w_2, \tag{S4}$$

w_{cryst} is determined from the Lorentzian fitting $L_{\mathrm{meas}}(w_{\mathrm{meas}})$ that models a measured XRD peak and the Lorentzian fitting $L_{\mathrm{inst}}(w_{\mathrm{inst}})$ that accounts for the instrumental broadening, as follows:

$$L_{meas}(w_{meas}) = L_{inst}(w_{inst}) \otimes L_{cryst}(w_{cryst}), \tag{S5}$$

$$w_{cryst} = w_{meas} - w_{inst}. \tag{S6}$$

Difference in $2\theta_{\mathrm{c}}$ between Cu-$K_{\alpha1}$ and Cu-$K_{\alpha2}$ diffractions from a given plane

As expected from Bragg's law:[S2]

$$\sin\theta_c = \frac{\lambda}{2d}, \tag{S7}$$

where d is the interplanar spacing of the crystallite, the difference in $2\theta_{\mathrm{c}}$ between Cu-$K_{\alpha1}$ and Cu-$K_{\alpha2}$ diffractions from a given plane is described as follows:

$$\Delta 2\theta_c = 2\theta_{c,Cu-K\alpha2} - 2\theta_{c,Cu-K\alpha1} = 2\left(\sin^{-1}\left(\frac{\lambda_{Cu-K\alpha2}}{2d}\right) - \sin^{-1}\left(\frac{\lambda_{Cu-K\alpha1}}{2d}\right)\right). \tag{S8}$$

The Cu-$K_{\alpha1}$ and Cu-$K_{\alpha2}$ diffractions from a plane that has a large d of 5.0 Å are, for example, expected to be observed in the small 2θ region around 17.7 ° with a small $\Delta 2\theta_{\mathrm{c}}$ of 0.044 °; whereas those from a plane that has a small d of 1.0 Å are expected to be observed in the large 2θ region around 100.8 ° with a large $\Delta 2\theta_{\mathrm{c}}$ of 0.345 °. This suggests that Cu-$K_{\alpha1}$ and Cu-$K_{\alpha2}$ diffractions can be readily separated in the large 2θ region, but cannot be separated in the small 2θ region.

Lorentzian fitting $L_{\mathrm{meas}}(w_{\mathrm{meas}})$ that models measured XRD peaks

Fig. S2(a) shows the XRD plot of the filtered substance, in the powder synthesis, annealed at 450 °C. The substance is identified as SnO, as described in the main manuscript. A magnified view of the SnO (001), (101), (211), and (220) diffraction at 2θ of 18.3, 29.9, 57.5, and 70.0 °, respectively, is presented in Figs. S2(b)-(e). As expected from Bragg's law consideration, the (001) and (101) diffractions in the small 2θ region are observed as a singlet peak that is modeled by a single Lorentzian fitting; whereas the (211) and (220) diffractions in the large 2θ region are observed as a doublet peak that is modeled by two Lorentzian fittings. The doublet peak is fitted by two Lorentzians with an integrated intensity ratio $A_{\mathrm{Cu}\text{-}K\alpha1}/A_{\mathrm{Cu}\text{-}K\alpha2}$ kept at a constant value of 1.82, which is determined from the (400) diffraction of a Si(100) substrate.

Lorentzian fitting $L_{\mathrm{inst}}(w_{\mathrm{inst}})$ that accounts for instrumental broadening

Fig. S3(a) shows the XRD plot calculated on the basis of the SnO reference pattern (ICDD-PDF: 01-072-1012) for the estimate of instrumental broadening. A set of diffraction pattern that corresponds to Cu-$K_{\alpha1}$ line is calculated for the SnO reference pattern and a XRD plot is simulated by convoluting the set of diffraction pattern with Lorentzians which have a FWHM of 0.055 °, as listed in Table S1. Another XRD plot that corresponds to Cu-$K_{\alpha2}$ line is also simulated in the same manner as in Cu-$K_{\alpha1}$ line. The two XRD plots are then superimposed at an integrated intensity ratio $A_{\mathrm{Cu}\text{-}K\alpha1}/A_{\mathrm{Cu}\text{-}K\alpha2}$ of 1.82. A magnified view of the (001), (101), (211), and (220) diffraction at 2θ of 18.3, 29.9, 57.5, and 70.0 °, respectively, is given in Figs. S3(b)-(e). The (001) and (101) diffractions in the small 2θ regions, in contrast to measured XRD peaks, are not observed as a singlet peak and cannot be qualitatively modeled by a single Lorentzian fitting; whereas the (211) and (220) diffractions in the large 2θ region are observed as a doublet peak that is modeled by two Lorentzian fittings, in the same manner as measured XRD peaks.

Estimate of SnO crystallite size d_{cryst}

The crystallite size is estimated for specific planes that meet the following conditions: (1) the XRD peak does not consist of diffractions from multiple planes but from a single plane; (2) the intensity of the XRD peak is high enough to be qualitatively modeled by Lorentzian fittings; and (3) both the measured and calculated peaks must be modeled by either a single Lorentzian or two Lorentzians to accurately calculate w_{cryst}. Since only the (211) and (220) planes fulfill those conditions, Cu-$K_{\alpha 1}$ diffractions from the two planes are chosen for the estimate of crystallite size d_{cryst} according to Scherrer's formula. Fig. S5 exhibits d_{cryst} as a function of annealing temperature, and Table S2 summarizes parameters extracted from the measured XRD plots, as shown in Figs. S2(d)-(e), and the calculated XRD plots, as presented in Figs. S3(d)-(e).

Table S1 Two Lorentzian fittings to doublet peak from (400) diffraction of a Si(100) substrate.

X-ray line	peak position,[a] $2\theta_c$ (°)	full-width at half maximum,[a] w (°)	integrated intensity, A (arb. units)
Cu-$K_{\alpha 1}$	69.138	0.0546	95332
Cu-$K_{\alpha 2}$	69.335	0.0568	52301

[a] The value is given in terms of 2θ.

Table S2 Parameters for the estimate of SnO crystallite size d_{cryst} in the case of the filtered substance, in the powder synthesis, annealed at a temperature of 450 °C.

plane	$2\theta_c$[a]	w_{meas}[a]		w_{inst}[a]		w_{cryst}[a]	d_{cryst}
	(°)	(°)	(radian)	(°)	(radian)	(radian)	(nm)
(211)	57.39	0.225	0.00393	0.0546	0.000953	0.00298	53.2
(220)	69.93	0.174	0.00303	0.0546	0.000953	0.00208	81.5

[a] The value is given in terms of 2θ.

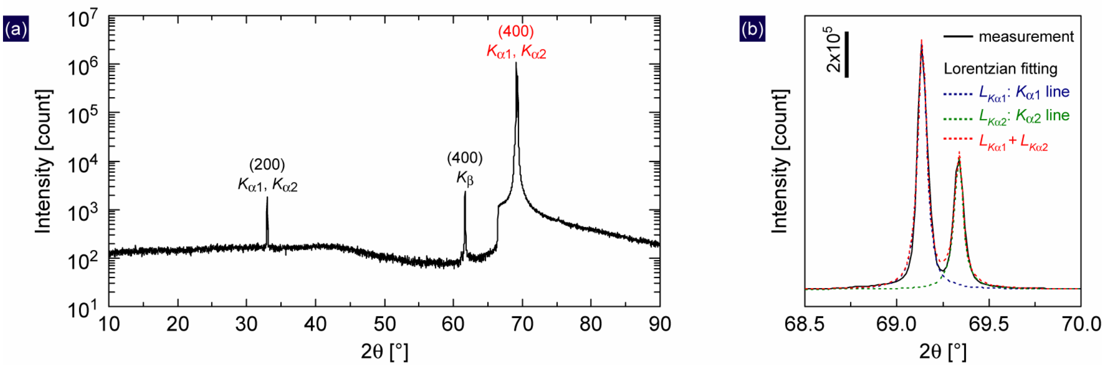


Fig. S1 (a) X-ray diffractogram of a Si(100) substrate with the intensity shown in a logarithmic scale. (b) Doublet peak from the (400) diffraction at 2θ of 69.1 °. The Lorentzian fitting in a dotted blue and green curve corresponds to the Cu-$K_{\alpha1}$ and Cu-$K_{\alpha2}$ diffraction, respectively, and the sum of the two fittings is given in a dotted red curve.

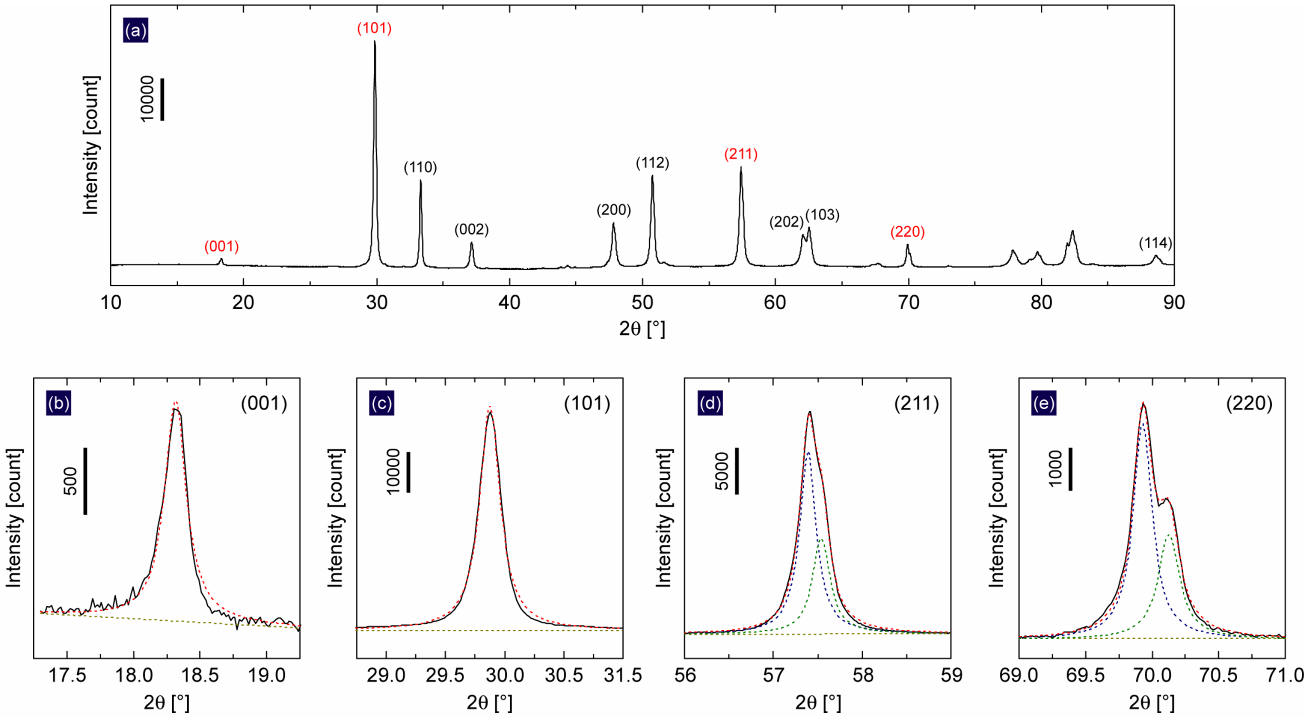


Fig. S2 (a) X-ray diffractogram of the filtered substance, in the powder synthesis, annealed at 450 °C. The substance is identified as SnO. (b)-(e) Peaks from (b) the (001) diffraction, (c) the (101) diffraction, (d) the (211) diffraction, and (e) the (220) diffraction. The background is shown in a dotted dark yellow line. A singlet peak in (b) and (c) is modeled by a single Lorentzian fitting in a dotted red curve. A doublet peak in (d) and (e) is modeled by two Lorentzian fittings that correspond to the Cu-$K_{\alpha 1}$ and Cu-$K_{\alpha 2}$ diffraction in a dotted blue and green curve, respectively, and the sum of the two fittings is given in a dotted red curve.

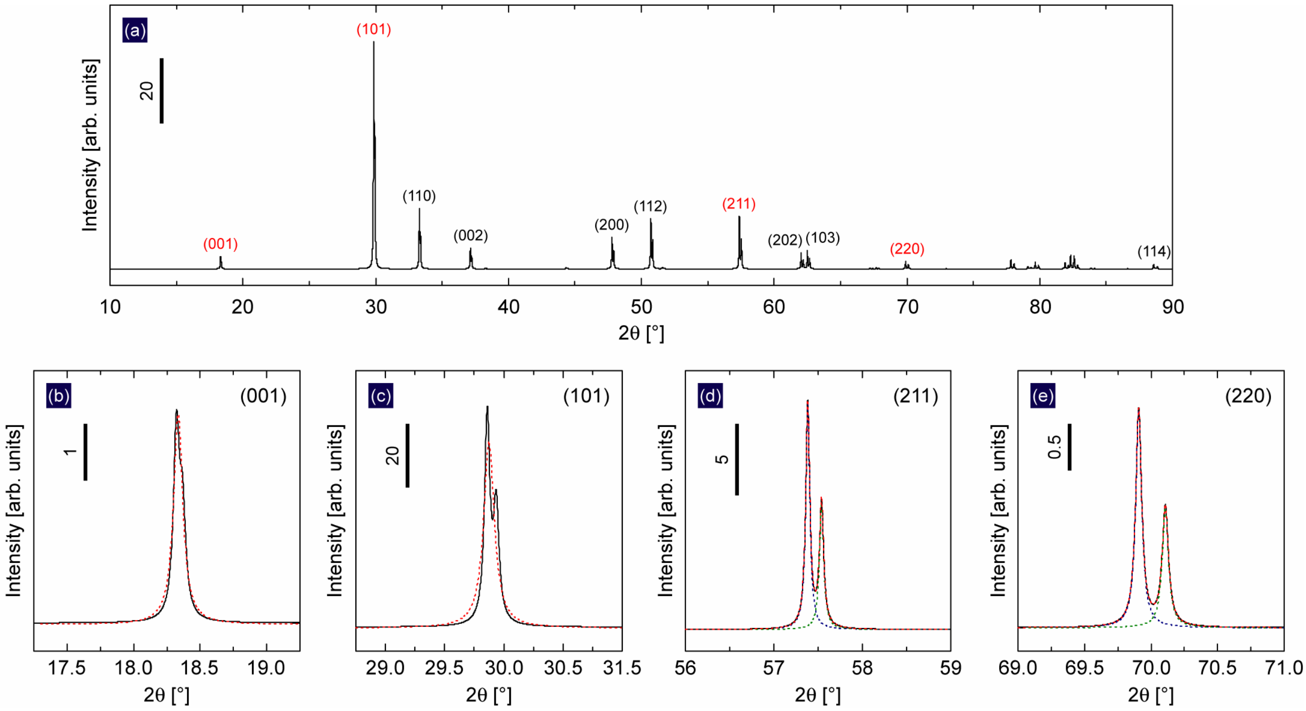


Fig. S3 (a) X-ray diffractogram calculated on the basis of the SnO reference pattern (ICDD-PDF: 01-072-1012) for the estimate of instrumental broadening. Two series of XRD patterns that correspond to Cu-$K_{\alpha1}$ and Cu-$K_{\alpha2}$ diffractions are taken into account and are superimposed at an integrated intensity ratio of 1.82. (b)-(e) Peaks from (b) the (001) diffraction, (c) the (101) diffraction, (d) the (211) diffraction, and (e) the (220) diffraction. A peak in (b) and (c) is modeled by a single Lorentzian fitting in a dotted red curve. A doublet peak in (d) and (e) is modeled by two Lorentzian fittings that correspond to the Cu-$K_{\alpha1}$ and Cu-$K_{\alpha2}$ diffraction in a dotted blue and green curve, respectively, and the sum of the two fittings is given in a dotted red curve.

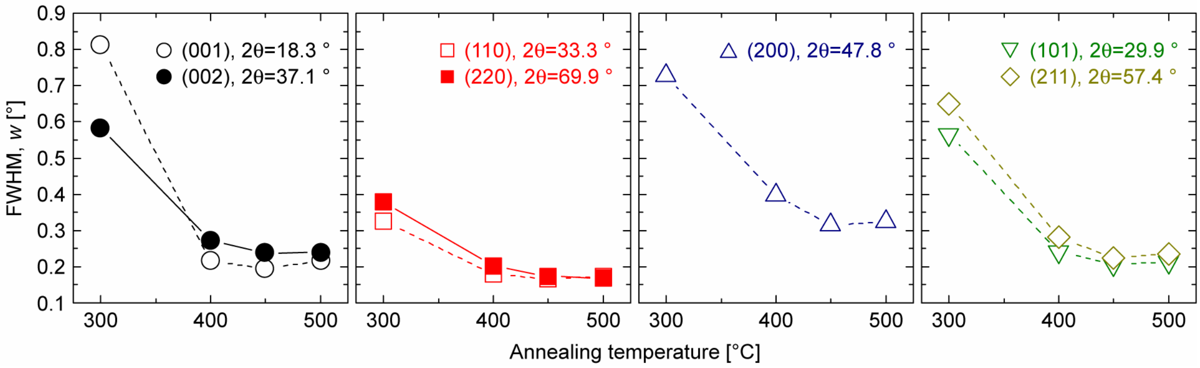


Fig. S4 FWHMs of the XRD peaks that correspond to SnO diffraction planes as a function of annealing temperature. The (001), (101), (110), (002), and (200) diffractions are modeled by a single Lorentzian fitting; while the (211) and (220) diffractions are modeled by two Lorentzian fittings, and FWHMs of the peaks that correspond to Cu-$K_{\alpha 1}$ diffractions are given in the figures.

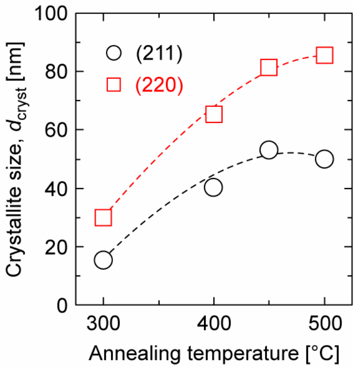


Fig. S5 SnO crystallite size d_{cryst} estimated from the (211) and (220) diffractions as a function of annealing temperature. Dashed curves are just guides for the eyes.

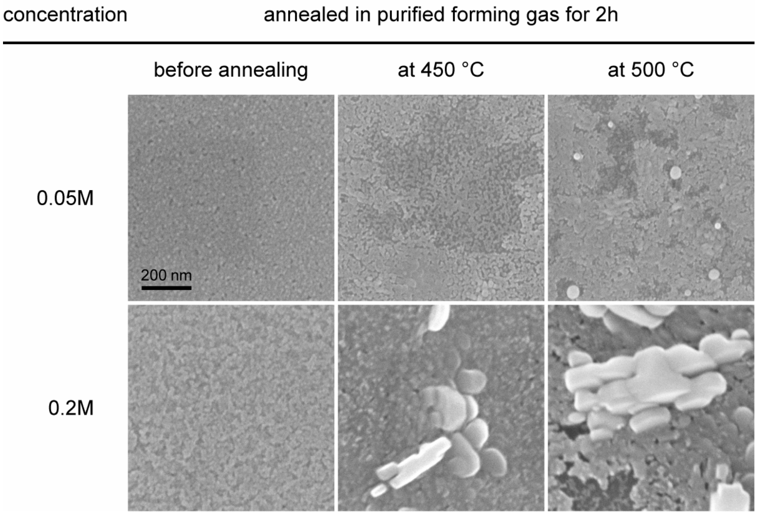


Fig. S6 SEM images of the thin films formed at a precursor concentration of 0.05 and 0.2 M and an annealing temperature of 450 and 500 °C.

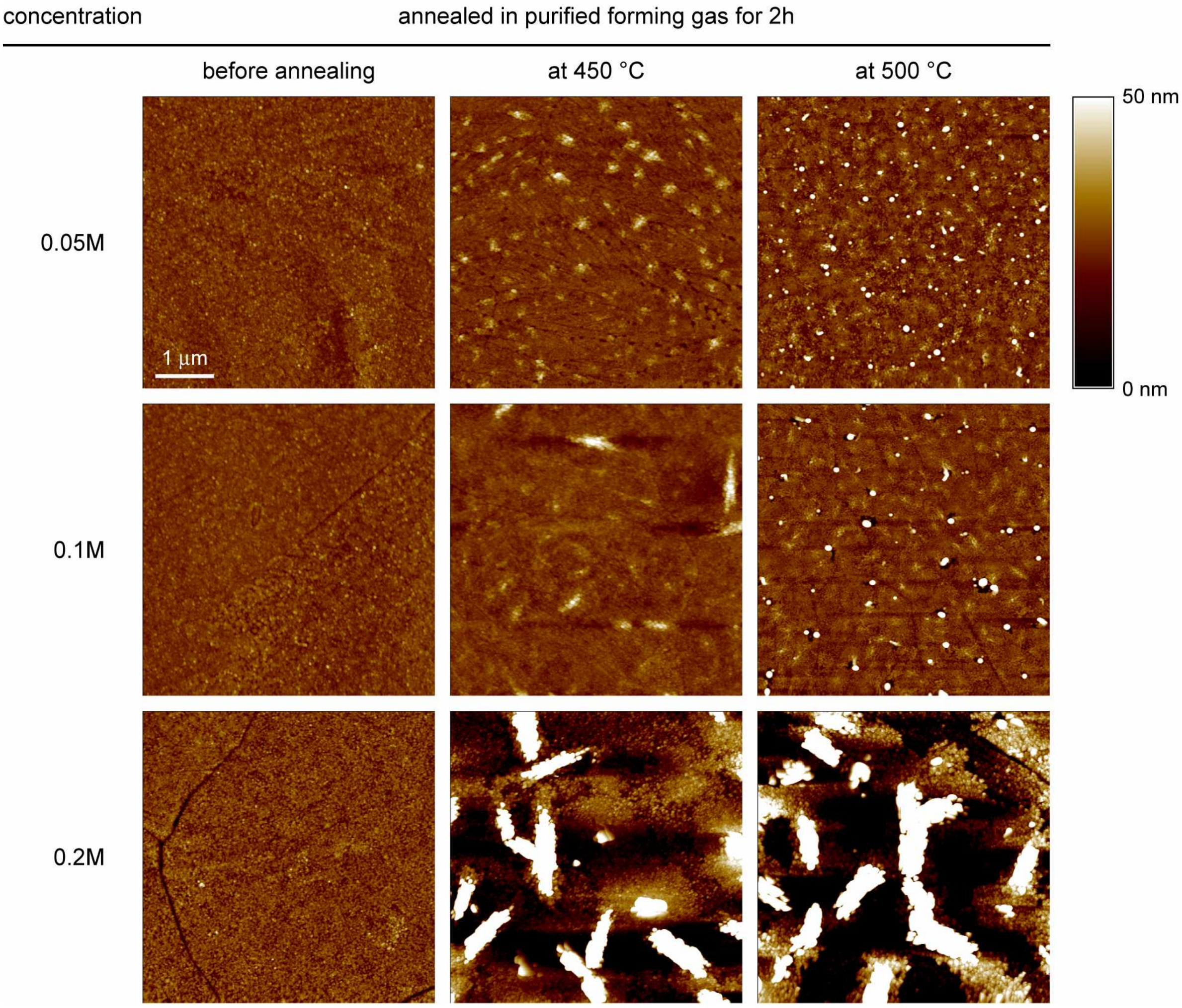


Fig. S7 AFM images of thin films formed at a precursor concentration of 0.05, 0.1, and 0.2 M and an annealing temperature of 450 and 500 °C.

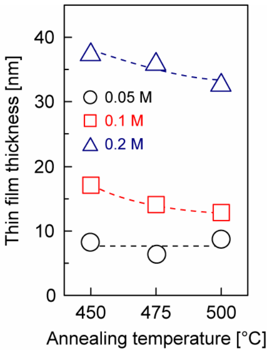
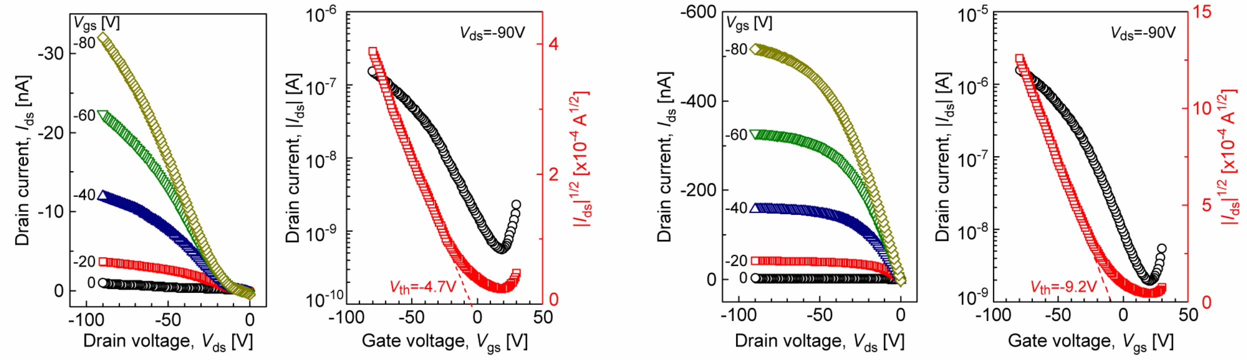
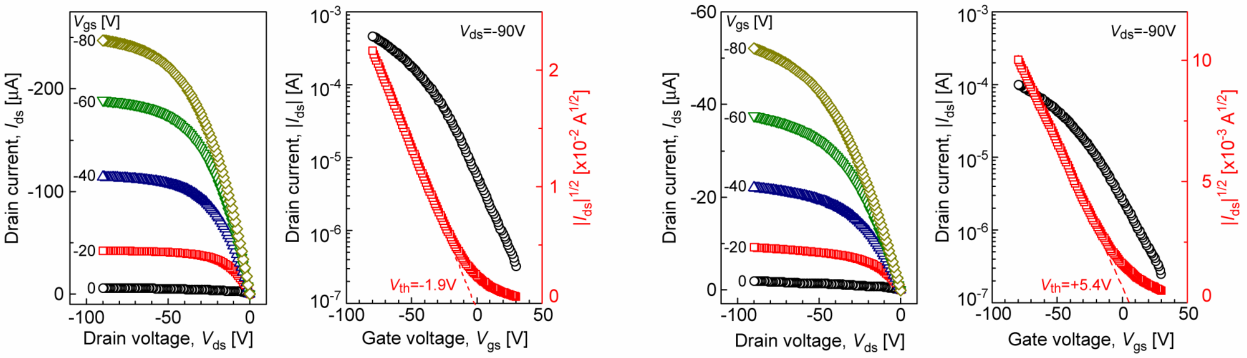


Fig. S8 Thickness of SnO thin films annealed at an indicated temperature as a function of the precursor concentration. The dashed curves are just guides for the eyes.

(a) 0.05 M and 450 °C (b) 0.05 M and 500 °C



(c) 0.1 M and 450 °C (d) 0.1 M and 500 °C



(e) 0.2 M and 450 °C (f) 0.2 M and 500 °C

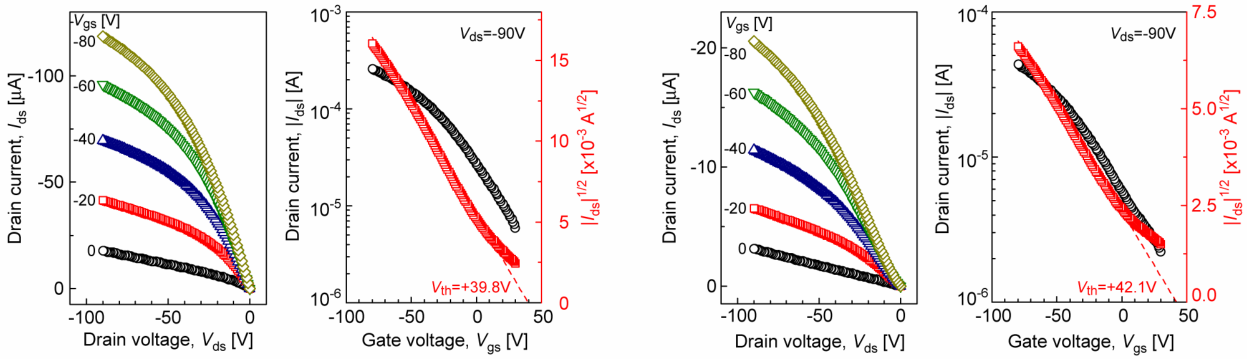


Fig. S9 *I*-*V* characteristics of the SnO TFTs formed at an indicated precursor concentration of 0.05-0.2 M and an indicated annealing temperature of 450-500 °C. The precursor concentration and annealing temperature are (a) 0.05 M and 450 °C, (b) 0.05 M and 500 °C, (c) 0.1M and 450 °C, (d) 0.1 M and 500 °C, (e) 0.2 M and 450 °C, and (f) 0.2 M and 500 °C, respectively.

References

[S1] S. M. Sze, *Physics of Semiconductor Devices 2nd Edition*, John Wiley & Sons, New York, 1981.

[S2] B. D. Cullity and S. R. Stock, *Elements of X-Ray Diffraction 3rd Edition*, Prentice-Hall, Inc., Upper Saddle River, 2001.