The Korean Journal of Ceramics, 6[4] 354-358 (2000)

Application of Inverse Pole Figure to Rietveld Refinement: III. Rietveld Refinement of SnO_2 Thin Film using X-ray Diffraction Data

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(Received July 5, 2000)

The SnO_2 film was deposited on a corning glass 1737 substrate by plasma enhanced chemical vapor deposition using a gas mixture of $SnCl_4$, O_2, and Ar. The film thickness was measured using α-step and was about 9400 Å. The conventional X-ray diffractometry and pole figure attachment were used to refine the crystal structure of SnO_2 thin film. Six pole figures, (200), (211), (310), (301), (321), and (411), were measured with CoK_α radiation in reflection geometry. The X-ray diffraction data were measured at room temperature using CuK_α radiation with graphite monochromator. The agreement between calculated and observed patterns for the normal direction of SnO_2 thin film was not satisfactory due to the severely preferred orientation effect. The Rietveld refinement of heavily textured SnO_2 thin film was successfully achieved by adopting the pole density distribution of each reflection obtained from the inverse pole figure as a correction factor for the preferred orientation effect. The R-weighted pattern, R_{wp}, was 15.30%.

Key words: Rietveld refinement, Plasma enhanced chemical vapor deposition, Preferred orientation, SnO_2 thin film, Inverse pole figure

I. Introduction

The powder diffraction method has been widely used as a non-destructive technique for identification, characterization of crystalline, and non-crystalline materials. It also provides information about structures, phases, preferred orientations, and other structural information, such as average grain size, crystallinity, strain, crystal defects, and so on. But the powder diffraction method always has been suffered from the disadvantage that an appreciable amount of structural information is lost owing to the overlaps of diffraction peaks. In spite of the demerit, with the spread or improvement of computers and the introduction of Rietveld refinement, the structural analysis using X-ray and neutron powder diffraction data has been become popular. Recently it has been recognized as a fundamental technique of characterization in the various fields.[1]

The sample in the Rietveld refinement should be composed of randomly oriented crystallites because the structural refinement in the Rietveld method is performed with a structural model given under the assumption that a sample consists of randomly oriented crystallites. But many kinds of technological materials made by the thermo-mechanical forming processes, such as compaction, settling, and deformation, inevitably produce the preferred orientation of the individual crystal grain. Particularly thin films or materials with layered structure are very difficult to satisfy the condition of starting structural model in the Rietveld refinement due to the preferred orientation or texture effect.[2]

If the crystallites in polycrystalline samples are not randomly oriented like an ideal powder sample, there is large deviation between the calculated and the observed intensities, because the observed intensity at each Bragg position is not only a function of crystal structure and instrument but also a function of texture or preferred orientation effect. When the Rietveld refinement is applied to the data showing the effect of preferred orientation, the Rietveld refinement results may be not available due to the texture effect. Therefore, to do Rietveld refinement for the preferred or textured polycrystalline samples, the effect of preferred orientation has to be corrected in some ways. The important point is how to correct the data involving the effect of preferred orientation or texture to get a good refinement results for the textured samples.[3-7]

In this paper we use the pole density for each reflection obtained from the inverse pole figure to carry out the Rietveld refinement for tin oxide (SnO_2) thin film. The SnO_2 thin film has been used for transparent electrode, display devices, solar battery, semiconductor sensor, etc. due to the two most outstanding properties, transparency and high conductivity.[8,9]

II. Experimental Procedure

The SnO_2 film was deposited on a corning glass by plasma enhanced chemical vapor deposition (PECVD) using a gas mixture of $SnCl_4$, O_2, and Ar. The deposition proceeded between parallel plates in a cold wall type vacuum chamber,

Table 1. Typical Deposition Conditions of SnO_2 Thin Film by PECVD

Deposition temperature	450°C
r. f. frequency	13.56 MHz
r. f. power	30 W
Deposition pressure	1 torr
P_{SnCl_4}	3.8×10^{-3} torr
P_{O_2}	5.6×10^{-1} torr

which was coupled with a radio frequency source. The upper electrode was connected to the radio frequency generator operating at 13.56 MHz while the lower one and reactor wall were grounded. Table 1 shows the typical deposition conditions of PECVD for SnO_2 thin film.

The inlet gas ratio of $SnCl_4$ and O_2 was controlled by varying both evaporating pressure and an amount of Ar gas passing through the evaporator of $SnCl_4$. The evaporator was maintained at 0°C for $SnCl_4$. The gas line to the reactor was heated up to 60°C to avoid the condensation of source vapor on the way.

The film thickness was measured using α-step (Dektak3 : Veeco sloan technology). The SnO_2 film thickness was about 9400 Å. The conventional X-ray diffractometry and pole figure attachment were used to measure the X-ray data of SnO_2 thin film. Six pole figures, (200), (211), (310), (301), (321), and (411), were measured with CoK_α radiation in reflection geometry. The pole figure data were measured over the orientation hemisphere within the α angles ranging from 0° to 70°, and the β angles ranging from 0° to 360°. The step interval was 5° for each α and β angles.

The X-ray diffraction data were measured at room temperature over scattering angle 20°~125° using CuK_α radiation with graphite monochromator. The step interval was at a 2θ of 0.02°. The X-ray diffracted intensities were measured by the θ-2θ scanning mode at the fixed normal direction of the sample. The sample was rotated during the measurement of X-ray diffraction. The Rietveld refinement was run with the RIETveld ANalysis (RIETAN) program, which was modified for the description of texture. The RIETAN program is a FORTRAN program developed by F. Izumi for the Rietveld refinement for X-ray, neutron, and synchrotron powder diffraction data.[10,11]

III. Results and Discussion

The X-ray diffraction pattern for SnO_2 thin film deposited at 450°C is shown in Fig. 1a. The observed d values agree with the values listed in Joint Committee on Powder Diffraction Standards (JCPDS card No. 41-1445) for SnO_2 powder (Fig. 1b).[12] However, the relative intensity for each peak did not agree well with the intensity data of JCPDS. The (110) plane in the case of SnO_2 powder has a maximum intensity, whereas the SnO_2 thin film has a strongest intensity corresponding to the (211) plane, which is the preferential orientation plane or texture axis. Some researchers

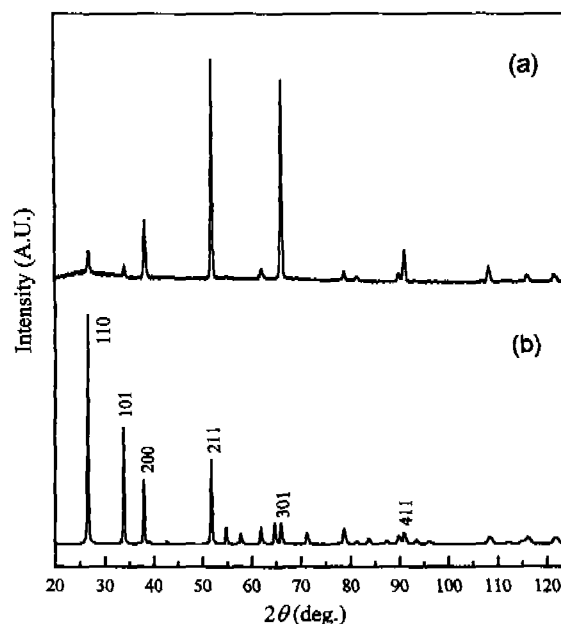

Fig. 1. X-ray diffraction patterns: (a) the observed X-ray diffraction pattern of SnO_2 thin film and (b) the calculated one for the randomly oriented SnO_2 powder sample.

have also found peaks of Sn_3O_4, and SnO phases in SnO_2 films using X-ray diffraction studies.[8,9] However, no such peaks in our sample were observed as shown in Fig. 1a. This means that SnO_2 thin film deposited by PECVD consists of a single phase.

From the observed diffraction pattern, the crystal structural parameters of SnO_2 thin film and various instrumen-

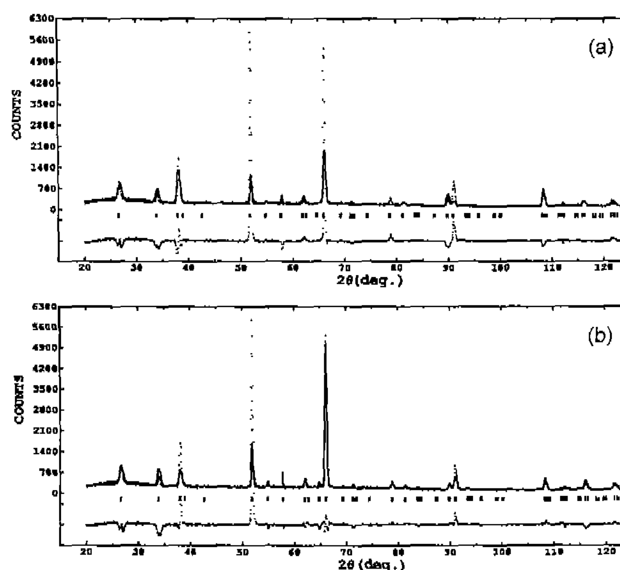

Fig. 2. The Rietveld refinement patterns: (a) without correcting the preferred orientation effect and (b) with the March-Dollase function. Dots represent the observed intensities, and the solid line is calculated ones. A difference (obs. - cal.) plot is shown beneath. Vertical bars are the reflection position markers.

tal parameters were refined with the Rietveld method, assuming that the sample is a powder with a random orientation distribution. The starting model was built by the crystallographic data reported by McCarthy and Welton (Tetragonal, $P4_2/mnm$, No. 136).[12]

Since the SnO_2 thin film is textured, it is not possible to obtain a good refinement pattern and there are positive and negative deviations in intensity as shown in the lower curve of Fig. 2a. The deviation is due to texture or preferred orientation effect. Therefore, in order to get a good Rietveld refinement result of SnO_2 thin film, some ways are required to correct the effect of texture.

Since the Rietveld program has been introduced, the description of texture has been an important part of the Rietveld refinement. The Rietveld programs are usually used the semi-empirical functions to correct the texture in the powder sample.[13,14] Of these functions, March-Dollase function based on the concept of rigid platy or acicular in a viscous medium has been widely used as a technique for correcting the preferred orientation effect :

$$P_k=\frac{1}{m_k}\sum_{j=1}^{m}(r^2\cos^2\alpha_j+r^{-1}\sin^2\alpha_j)^{-3/2}$$

where α_j is the angle between the preferred orientation direction and jth member of the symmetry-equivalent set of m_k diffraction planes. The variable parameter, r, March-Dollase coefficient, represents the effective sample compression or extension due to the preferred orientation effect. It shows the best overall performance crystal structures studies and can be used in quantitative phase analysis.

Fig. 2b shows the Rietveld refinement pattern using the March-Dollase function. Compared with the Rietveld refinement pattern without the March-Dollase function, the agreement between the observed and calculated patterns was improved. However, the intensity difference between the observed and calculated intensities was still large as shown in Fig. 2b. It is clear that the March-Dollase function is inadequate to the SnO_2 thin film sample.

In order to correct the texture effect of the SnO_2 thin film sample, we, therefore, tried to use the pole density for each

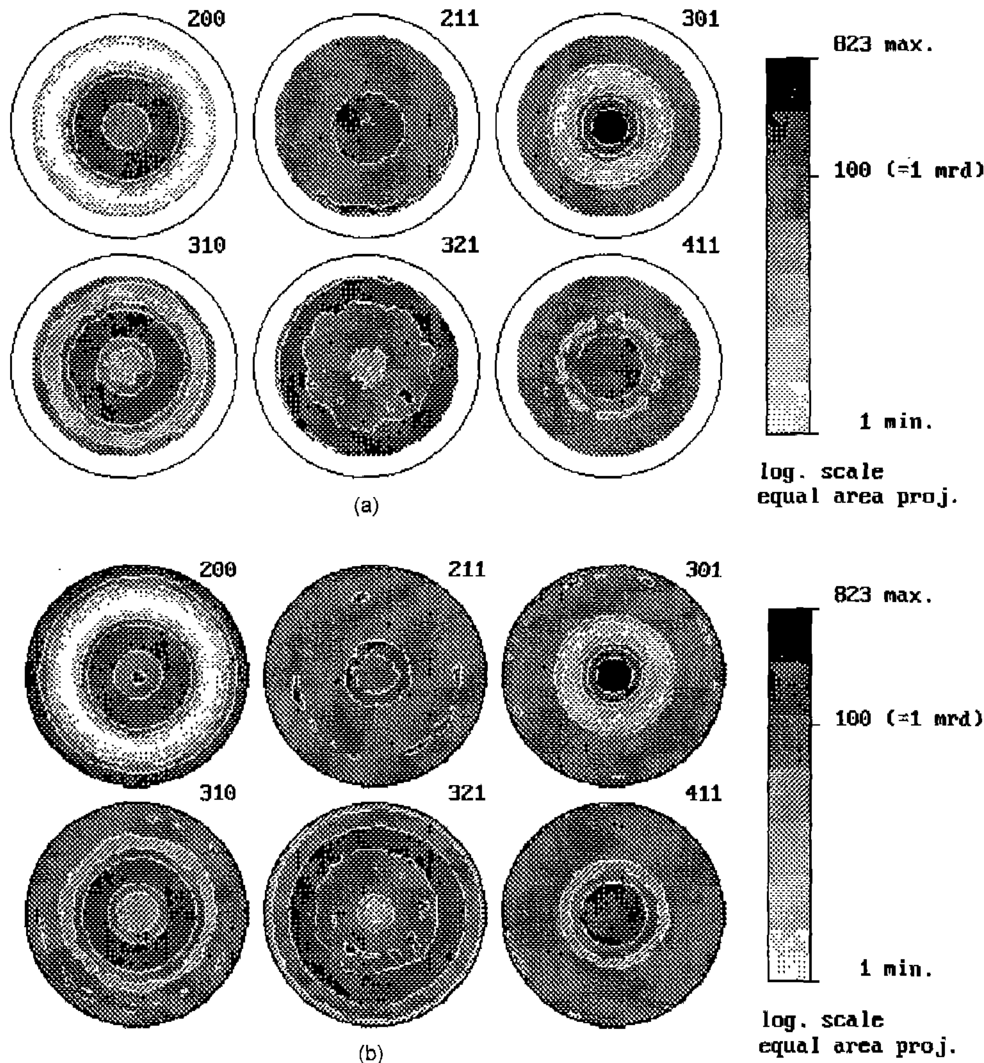

Fig. 3. Pole figures of SnO_2 thin film: (a) experimental and (b) recalculated pole figures.

reflection because the effect of texture on the diffraction pattern may be directly proportional to the pole density of the corresponding inverse pole figure.[4,5)] The pole density for each reflection in a sample can be obtained from quantitative texture analysis. The quantitative texture analysis is to determine orientation distribution of crystallites or orientation distribution function (ODF) in a polycrystalline sample from experimental pole figure data. The ODF analysis requires several experimental pole figure data for each pole distance and azimuthal angle. The ODF describes the probability density of crystallites that have the orientation within unit volume in a polycrystalline sample. It is derived from experimental pole figure data, which is measured by X-ray or neutron diffraction techniques, using the harmonic, vector, and Williams-Imhof-Matthies-Vinel (WIMV) methods.[14,15)]

The pole figure data of six reflections, (200), (211), (310), (301), (321), and (411), were measured with the pole figure attachment in reflection geometry. The ODF was calculated by the WIMV algorithm, using popLA program.[16)] Triclinic sample symmetry was used for the texture analysis. The experimental and recalculated pole figures for six reflections are shown in Fig. 3. The agreement between the experimental and the recalculated pole figures was satisfactory. The inverse pole figure of the normal direction was calculated by the ODF (Fig. 4).

Table 2 lists the pole densities extracted from the inverse pole figure. In Table 2, the pole density value of 301 reflection is significantly higher than that of other ones, which is well in agreement with the relative intensity of 301 reflection in the observed pattern as shown in Fig. 2a. Applying the pole density for each reflection to the observed diffraction data, the calculated diffraction pattern was very nearly identical with that in the observed ones. This means that the correcting approach of texture effect in terms of the inverse pole figure can be applicable to the Rietveld refinement of SnO_2 thin film.

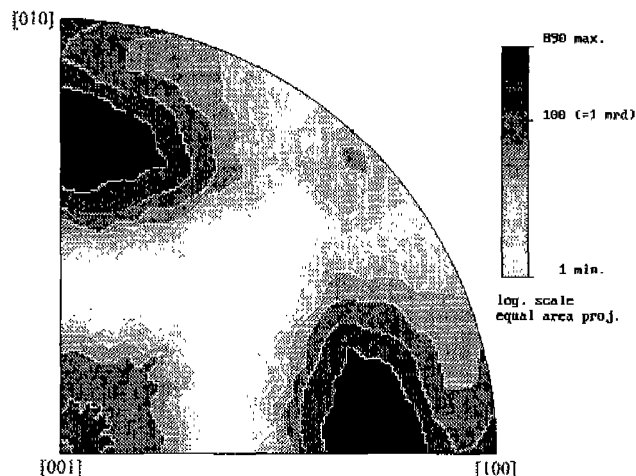

Fig. 4. Inverse pole figure of SnO_2 thin film of the normal direction. Equal-area projection; levels are in multiples of random distribution.

Table 2. Pole Densities Obtained from the Inverse Pole Figure of the Normal Direction

hkl	mrd [i)]	hkl	mrd	hkl	mrd
110	0.1100	101	0.4900	200	1.8000
111	0.0010	210	0.0443	211	0.5208
220	0.1100	002	1.0800	310	0.2983
221	0.0137	112	0.0010	301	8.4397
311	1.0109	202	0.4900	320	0.0174
212	0.1193	321	0.0451	400	1.8000
222	0.0010	410	0.4931	312	3.1074
411	0.6807	420	0.0443	331	0.1196
103	0.5497	322	0.1079	113	0.6394
421	0.1794	213	0.0010	402	4.4904
430	0.0312	412	4.6123	510	0.5586
332	0.0010	501	1.5791	431	0.0369
223	0.0010	511	0.4792	303	0.4900
422	0.5208	520	0.1624	313	0.3362
521	0.3147	440	0.1100		

i) mulitiples of random distribution

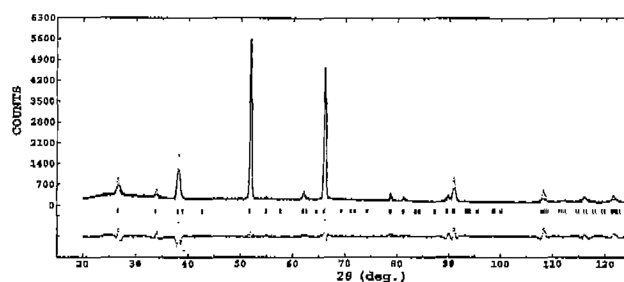

Fig. 5. Rietveld refinement pattern of SnO_2 thin film using the pole densities obtained from the inverse pole figure. Dots represent the observed intensities and the solid line is calculated ones. A difference (obs.-calc.) plot is shown beneath. Vertical bars are the reflection position markers.

The texture effect was corrected with the pole densities of all reflections and then the initial refinement was done by the unit-cell, the zero point shift, scale factor, and background parameters. A good match of the peak positions was achieved from the preliminary refinement and then the peak profile parameters including the peak asymmetry parameter were refined. The Rietveld refinement is dramatically improved. Finally, the weight R-factor, R_{wp}, and the goodness-of-fit values, S $(=R_{wp}/R_e)$, was decreased to 15.30% and 2.48, respectively. The agreement between observed and calculated patterns was very satisfactory as shown in Fig. 5.

Evidently, these low R-factors and S could be obtained by applying the pole density for each reflection to the observed data as a correction factor of texture. These results support that the approach based on the texture analysis may be expected to become an alternative to the Rietveld refinement with empirical functions, particularly, in the case of samples showing strong texture.

Final crystal data and selected interatomic distances of SnO_2 thin film are given in Table 3 and Table 4, respec-

Table 3. Structural Parameters Obtained for SnO_2 Thin Film at the Room Temperature
R_{wp}=15.30%, R_p=11.05%, R_I=8.33%, R_F=6.71% and S (=R_{wp}/R_e) =2.48. $a=b$=4.7365(20) Å and c=3.2010(13) Å. Symbol g is the Occupation Factor

Atom	Site	x	y	z	g	B (Å^2)
Sn	2*a*	0	0	0	1.0	0.2(4)
O	4*f*	0	0	0.307(14)	1.0	0.25(21)

Table 4. Selected Interatomic Distances in SnO_2 Thin Film. Symbol m is the Multiplicity of Each Distance

Bond	l (Å)	m
Sn-O[i]	1.949(5)	4
Sn-O	2.001(3)	2
Sn-Sn[i]	2.965(2)	4
O-O[i]	2.490(4)	2
O-O[ii]	2.821(9)	2
O-O[iii]	3.798(2)	4

Symmetry codes: i) x,1/2 + y, 1/4 z; ii) 1/2 + y. 1/2 + x, 1/2 z; iii) y, 1/2 + x, 1/4 + z

tively. The SnO_2 thin film deposited by PECVD did not show a mechanical strain for the normal direction because the unit cell is nearly identical with one of SnO_2 powder, which is reported by McCarthy and Welton.[12]

IV. Conclusion

The SnO_2 film was deposited on a corning glass 1737 substrate by plasma enhanced chemical vapor deposition using a gas mixture of $SnCl_4$, O_2, and Ar. The diffraction pattern for the normal direction of SnO_2 thin film surface showed entirely different intensity profiles because of the severe preferred orientation effect. The Rietveld refinement of heavily textured SnO_2 thin film was successfully achieved by adopting the pole density distribution of each reflection obtained from the inverse pole figure as a correction factor for the preferred orientation effect. This approach offers the possibilities for the Rietveld refinement of heavily textured polycrystalline materials like thick or thin films. In addition, this works shows that it may be used in the determination of quantitative phase analysis and residual stresses of textured materials.

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