X- RAY DIFFRACTION LINE PROFILE ANALYSIS OF STRONGLY TEXTURED THIN FILMS

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1   Introduction

Thin films of metallic conductors, semiconductors and insulators are the basic materials for modern electronic devices. For optimal device performance, these films should possess specific mechanical, electrical, magnetic or optical properties which are strongly influenced by the microstructural qualities of the films such as crystalline or amorphous state, crystallographic orientation, crystallite size, strain and stresses. Therefore, microstructural characterization of thin films is very important for the design and improvement of electronic devices 1.

Due to their small dimensions perpendicular to the surface, the microstructure of thin films cannot be easily characterized by methods developed for the bulk materials. Therefore, various methods of surface physics are frequently applied to thin films. Among the analytical methods especially suitable for thin films, X-ray diffraction plays an important role since it is nondestructive, noncontact and highly quantitative.

However, due to the thinness of the film the diffracting volume is normally very small resulting in weak diffracted intensities. On the other hand, due to preferred orientation of crystallites in a certain direction, some diffraction lines can reach very strong intensities so that in such case there is no problem to apply line profile analysis to obtain the basic structural characteristics of thin films.

In line profile analysis mainly broadening and shape of diffraction line are investigated. Broadening of X-ray diffraction line profiles is mainly caused by nonideal optics of the instrument, wavelength dispersion and structural imperfections of the specimen. The structural line broadening is often subdivided into size broadening and strain broadening. Size broadening is caused by the finite size of domains diffracting essentially incoherently with respect to one another. On the other hand, strain broadening is caused by varying displacements of the atoms with respect to their reference-lattice positions [2].

Line broadening is frequently characterized by means of one or two breadth measures (FWHM - full width at half maximum and β = Area/I_o - integral breadth) and separation of size and strain contributions has been performed on this basis [3, 4]. More detailed analysis is possible by taking into account the complete shape of a line profile by expressing it in terms of Fourier coefficients. Both breadth

and Fourier methods gain in reliability when more than one order of reflection is used for a given set of lattice planes [5].

2   Experimental procedure

In our work, ceramic and metallic thin films deposited on single-crystalline silicon wafers by means of diode sputtering were investigated. In special cases Pd, Ti, Al, SiO_2 and Al_2O_3 buffer layers were also applied. A planar r.f. sputtering system Perkin Elmer 2400/8L was used. The sputtering chamber was always pumped down to $2x10^{-5}$ Pa before admission of working gas (Ar or Ar/O_2 gas mixture 99.999% in purity). Throughout the sputtering of Ag, Pd, Pt, Al, ZnO and Al_2O_3 targets (each 203 mm in diameter and 99.95% in purity) a gas pressure of 1.3 Pa was kept constant [6, 7]. The temperature of substrate was mostly kept at room temperature. In special cases the temperature of substrate was kept at 300^oC or at 600^oC. The effects of different r.f. powers, different substrates, different metallic materials with a FCC cubic unit cell and different film thicknesses were investigated. Furthermore, different ratios of Ar/O_2 gas mixture in case of ZnO films as well as the cyclic sputtering and ion etching of films were applied [8, 9]. The general characterization of sputtered films is listed in Table 1.

X-ray diffraction line profile analysis was used to determine microstructural properties of investigated films. First, preliminary diffraction patterns was recorded on the film. After that, the X-ray diffraction data were collected by using an automatic X-ray powder diffractometer URD-6 with a Bragg-Brentano goniometer. A copper X-ray tube (λ= 0.154178 nm) was used. Ceramic Al_2O_3 from NIST was used as an instrumental standard. The intensities of diffraction lines were collected with a constant step of 0.02 deg of 2-theta and with a constant counting time of 20 seconds at each step. In order to appreciate degree of preferred orientation, the omega-scans of the most intensive diffraction lines for each material were also recorded.

From several available methods appropriate for the line profile analysis a single-line method based on a Voigt function [3] which is more versatile and powerful from the practical point of view was used to determine size-strain parameters (microstrains and crystallite sizes) of investigated thin films 4]. Because no monochromator was used,

Table 1. Characterization of investigated thin films

Sample (thin film)	Special conditions	Substrate (configuration)	R.f. Power [W]	Thickness [nm]	Substrate temperature [^{O}C]
ZnO 1	Ar+O$_2$ (25/75)	Al/SiO$_2$/Si	500	1000	room
ZnO 2	Ar+O$_2$ (25/75)	SiO$_2$/Si	500	1000	room
ZnO 3	5x etch	Al/SiO$_2$/Si	500	1000	room
ZnO 4	5x etch	SiO$_2$/Si	500	1000	room
ZnO 5	Ar+O$_2$ (60/40)	Al/SiO$_2$/Si	500	1000	room
ZnO 6	Ar+O$_2$ (60/40)	SiO$_2$/Si	500	1000	room
Zn$_x$O$_y$ 1	Multilayers	Al$_x$O$_y$/SiO$_2$/Si	500	250	room
Zn$_x$O$_y$ 2	Multilayers	Al$_x$O$_y$/SiO$_2$/Si	500	250	300
Zn$_x$O$_y$ 3	Multilayers	Al$_x$O$_y$/SiO$_2$/Si	500	250	600
Ag 1	Ar	Pd/Ti/SiO$_2$/Si	250	1000	room
Ag 2	Ar	Pd/Ti/SiO$_2$/Si	500	1000	room
Ag 3	Ar	Pd/Ti/SiO$_2$/Si	800	1000	room
Ag 4	Ar	SiO$_2$/Si	500	1000	room
Ag 5	Ar	Si [100]	500	1000	room
Pd	Ar	Si [100]	500	1100	room
Pt	Ar	Si [100]	500	1000	room

the K$_{\alpha 2}$ line had to be removed by a Rachinger method (in case of broad lines of ZnO and Pt films) and by a graphic method 10, 11] modified for a processing on a personal computer (in case of narrow lines of metallic Ag and Pd films).

3   Results and Discussion

Because Zinc Oxide has a hexagonal close-packed wurtzite structure, polycrystalline thin films prepared by different techniques have usually preferential orientation of their grains in the [001] direction perpendicular to the substrate, strongly depending on the deposition conditions in the deposition unit.

Diffraction patterns preliminary recorded on the film indicated that all investigated films were polycrystalline. Almost in all cases, a very strong preferred orientation of crystallites perpendicular to the substrate, depending on the material and on the special conditions in the course of deposition, was observed. In case of zinc oxide films the preferred orientation is mainly in the [001] and [110] directions and in case of metallic films (Ag, Pd, Pt) it is in the [111] direction (See part of ZnO X-ray diffraction patterns presented in Figures 1, 2, 3 and 4).
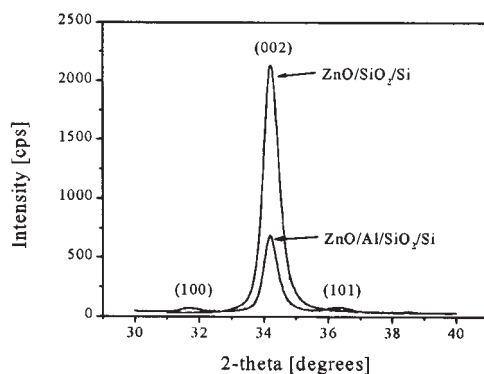

Figure 1. Influence of aluminium buffer layer on preferred orientation of ZnO film (Ar/O$_2$=25/75 %)
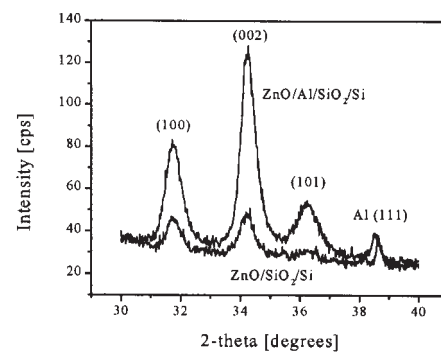

Figure 2. Influence of cyclic sputtering and ion etching of films on preferred orientation of ZnO films (Ar/O$_2$ = 25/75 %)

Table 2 Data of investigated thin films obtained from X-ray diffraction

Sample (thin film)	Investigated line	Line position	Intensity of $K_{\alpha 1}$[cps]	FWHM [deg]	Integrated intensity [deg/s]
ZnO 1	002	34.184	436	0.4825	282.8
ZnO 2	002	34.205	1467	0.5568	1052
ZnO 3	110	56.265	101	0.9765	119.4
ZnO 4	110	56.324	279	1.0537	359.4
ZnO 5	002	34.216	1664	0.4591	1016
ZnO 6	002	34.027	2445	0.7335	2218
Zn$_x$O$_y$ 1	002	34.265	5.9	0.4453	3.3
Zn$_x$O$_y$ 2	002	34.379	32.47	0.5799	24.4
Zn$_x$O$_y$ 3	002	34.372	724.4	0.4254	365.7
Ag 1	111	38.128	2428	0.0607	201.0
Ag 2	111	38.109	4345	0.0559	320.1
Ag 3	111	38.109	8781	0.0594	686.9
Ag 4	111	38.103	1980	0.0550	154.8
Ag 5	111	38.142	3527	0.0682	336.2
Pd	111	40.197	1548	0.0790	172.4
Pt	111	39.776	2.2277	0.2076	6272

Table 3 Size-strain data of investigated thin films

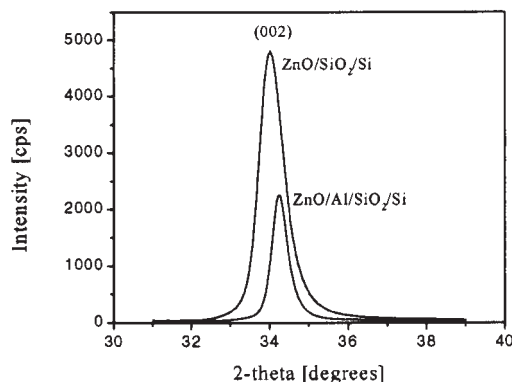| Sample (thin film)	Investigated line	Integral breadth [deg] β	Shape factor ϕ=FWHM/β	Microstrains $\langle\varepsilon\rangle$x10^3	Crystallite size D [nm]
ZnO 1	002	0.6493	0.7432	4.5	26
ZnO 2	002	0.7171	07764	5.9	28
ZnO 3	110	1.1818	0.8263	6.9	25
ZnO 4	110	1.2897	0.8170	7.3	21
ZnO 5	002	0.6104	0.7522	4.5	29
ZnO 6	002	0.9070	0.8087	8.6	27
Zn$_x$O$_y$ 2	002	0.7462	0.7772	6.2	27
Zn$_x$O$_y$ 3	002	0.548	0.8427	5.3	97
Ag 1	111	0.0828	0.7329	0.24	320
Ag 2	111	0.0737	0.7591	0.27	561
Ag 3	111	0.0782	0.7593	0.32	479
Ag 4	111	0.0782	0.7493	0.21	494
Ag 5	111	0.0952	0.7166	0.27	218
Pd	111	0.1115	0.7084	0.28	158

Figure 3. Influence of O_2 content in gas mixture on preferred orientation of ZnO film (Ar/O_2=60/40 %)
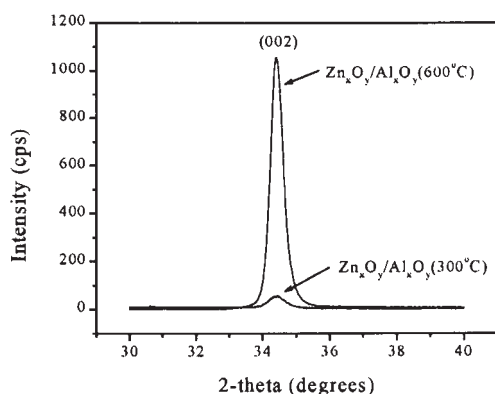

Figure 4. Influence of substrate temperature on preferred orientation of Zn_xO_y/Al_xO_y multilayered structures (Ar/O_2 = 25/75 %)

In case of continual sputtering there is a [001] preferred orientation of crystallites perpendicular to the substrate. Cyclic sputtering and ion etching of films in the course of deposition with 75% of O_2 content in the Ar/O_2 gas mixture resulted in [110] preferred orientation of ZnO grains perpendicular to the substrate. After cyclic sputtering and ion etching of films with 40% O_2 content in the Ar/O_2 gas mixture a very strong preferred orientation of ZnO crystallites in the [001] direction perpendicular to the substrate was observed again.

The aluminium conductive layer resulted in a decrease of preferred orientation of ZnO crystallites (Figures 1 and 3) as well as decrease of lattice imperfections, which can be observed in decreasing of microdeformations. Furthermore, in all cases of ZnO films a considerable shift of (002) and (110) diffraction lines towards the less diffraction angles was observed (See Table 2). Regular positions of (002) and (110) ZnO lines according to JCPDS standard are 34.44 and 56.55 deg respectively. This line displacement is accompanied with the lattice strains which are present in the ZnO films due to lattice mismatch between the layer and substrate and due to the low-energy ion bombardment of films.

The texture evolution depending on the substrate temperature during the deposition can be demonstrated on Zn_xO_y/Al_xO_y multilayered structures prepared as sensitive layers for UV radiation. When substrate temperature during the deposition was kept below 300°C, a part of amorphous phase was also observed. Much better preferred orientation was observed when substrate temperature was kept on 600°C (See Figure 4 and Table 2).

The most expressive preferred orientation of crystallites in the [111] direction perpendicular to the substrate was observed in case of metallic Ag, Pd and Pt films. These films are suitable materials for chemical and bio-chemical sensors as catalytic metal layers or as reference electrodes. XRD-scans of (111) lines are demonstrated in Figures 5, 6 and 7.
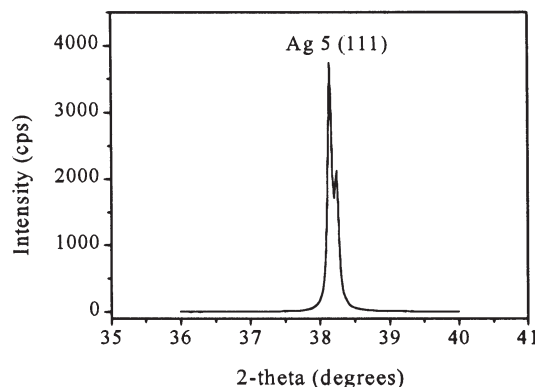

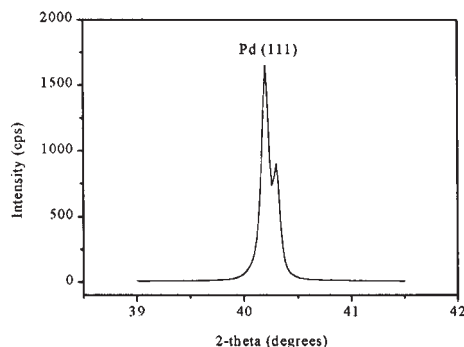**Figure 5.** XRD-scan for (111) line of Ag film deposited on single crystalline Si [100] substrate

Figure 6. XRD-scan for (111) line of Pd film deposited on single crystalline Si [100] substrate

In this case, only (111) line and its second order were observed. Degree of preferred orientation can be partially appreciated by the width of the omega-scans of (111) lines. The widths of the omega-scans for (111) lines of investigated Ag and Pt films are about 3.3-3.7 deg. For Pd film it is about 6.4 deg. Higher r.f. power applied in the sputtering unit resulted in a higher degree of preferred orientation of crystallites.

4   Conclusions

Our experiments indicated that the X-ray diffraction line profile analysis carried out on a common X-ray powder diffractometer can be successfully used when investigating the microstructural properties of strongly textured thin
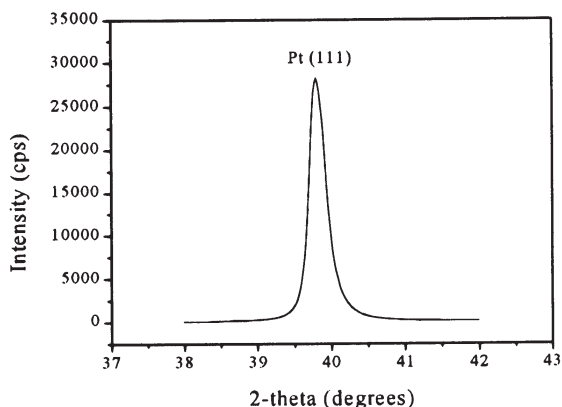
Figure 7. XRD-scan for (111) line of Pt film deposited on single crystalline Si [100] substrate
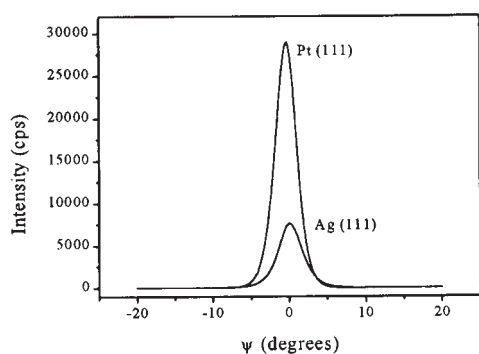

Figure 8. Omega-scans for (111) lines of Pt and Ag films deposited on single crystalline Si [100] substrate

films. The analysis is successful also in case when the film thickness is more less than one micrometer. More attention has to be paid to the narrow lines because in case of their approximation by a non-appropriate profile the results can be over- or underestimated.

Acknowledgements

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