ISSN 1027-5495. Functional Materials, 30, No.3 (2023), p. 338-343.
doi:https://doi.org/10.15407/fm30.03.338

Aluminum doped zinc oxide thin films with lower activation energy prepared by radio frequency magnetron sputtering

Sana Ullah

Institute of Mechanical and Manufacturing Engineering, Khwaja Fareed University of Engineering and Information Technology, Rahim Yar Khan, Pakistan

Received February, 3, 2023

Thin films of aluminum-doped zinc oxide (AZO) with reduced activation energy have been obtained and studied. Thin aluminum-doped zinc oxide films were grown by RF magnetron sputtering on silicon and glass substrates with different oxygen content in working gases ($Ar + O_2$). It was found that the activation energy of aluminum-doped zinc oxide films is about 0.03 eV and varies with the oxygen content.

Keywords: aluminium zinc oxide, zinc oxide, *n*-type materials, activation energy, doping, magnetron sputtering.

Тонкі плівки оксиду цинку, легованого алюмінієм з меншою енергією активації, отримані методом магнетронного радіочастотного розпилення. *Sana Ullah*

Отримано та досліджено тонкі плівки легованого алюмінієм оксиду цинку (AZO) зі зниженою енергією активації. Тонкі плівки оксиду цинку, леговані алюмінієм, були вирощені методом радіочастотного магнетронного розпилення на кремнієвих і скляних підкладках з різним вмістом кисню в робочих газах ($Ar + O_2$). Виявлено, що енергія активації плівок оксиду цинку, легованих та змінюється залежно від вмісту кисню.

1. Introduction

ZnO is an *n*-type broadband gap II–VI compound semiconductor. Recently ZnO has attracted increasing interest of the research and scientific community due to its tremendous potential [1]. It is a probable material for blue/UV optoelectronics [2], light-emitting [3] and also for laser diodes [4]. ZnO is a material with a direct band gap of about 3.4 eV and crystallises preferentially in the hexagonal wurtzite structure [5]. ZnO provides greater radiation resistance when used in electronic devices in an equivalent environment [6]. It is also considered as a candidate material for electronic circuits and as a diluted or ferromagnetic material for semiconductor spintronics [7]. It could also be a cheaper alternative to indium tin oxide (ITO) as a transparent and highly conducting oxide (TCO) material [8]. Another well-known semiconductor material that is widely used for the production of ultraviolet and light emitting diodes is GaN (Gallium Nitrate). ZnO has many advantages over GaN and is being considered as an alternative [9]. GaN is available in bulk and single crystal form and has direct band gap energy of 3.3 eV at 300 K [5]. Its large exciton binding energy (~ 60 meV) [5] promotes more efficient optical emission and detection at room temperature. The availability of its native substrate is good for the growth of homo-epitaxial thin films and devices. Much simpler crystal growth technology along with lower cost of the basic materials has resulted in potentially low cost ZnO devices. ZnO is found to be harder and its radiation resistance is much higher than GaN, which makes it a promising material for

UV detectors and emitters [10–11]. The better control over quality and conductivity of bulk and layered ZnO gives advantage for use of this material for short wavelength light [12] and transparent devices [13]. ZnO n-type conductivity is further enhanced by its doping with group-III elements such as Al, Ga and I [14–16]. AZO thin films have been prepared by many different techniques. AZO is emerging as an alternative to other TCOs [17], not only due to its comparable electro-optical properties, but also due to its cost effectiveness (with inexpensive, abundant raw materials), environment permissible nature (as non-toxic material) and more chemical, thermal stability than indium tin oxide (ITO) in reducing atmospheres. It is also reported that AZO films are more easily etched and prepared on relatively low-temperature substrates [18].

In a variety of works reported hereafter, different precursors have been used to prepare thin films with different dopants and dependence of optoelectronic properties including activation energy on deposition conditions and dopants have been reported. $BaSnF_4$ thin films doped with yttrium were prepared [20] and it was established that an increase in the content of the dopant, i.e., yttrium, lead to an increase in conductivity and a decrease in the activation energy. In another work, aluminium doped zinc oxide thin films were deposited at room temperature [21], and their optoelectronic properties were found to depend on the oxygen content during the process. In yet another work, P–N co-doped ZnO thin films were deposited by radio frequency sputtering [22], wherein electrical properties were found to depend on annealing temperature. Resistivity of the aluminium doped zinc oxide thin films prepared by sputtering [23] was controlled by the self-bias during the deposition. It has been observed that the deposition of thin AZO films using a ZnO seed layer [24] affects the carrier mobility and electrical conductivity. Similarly, transparent and conducting AZO thin films were deposited on soda-lime glass [25], and optoelectronic properties were examined. Structural and optical properties of ZnS thin films prepared by magnetron sputtering at different substrate temperatures were investigated in [26]. ZnO thin films have also been prepared by chemical bath deposition [27] and the influence of solution precursors have been observed. Single phase solid solutions of PbNaNdVO were prepared [28] and the values of activation energy were found to depend on both the composition and temperature.

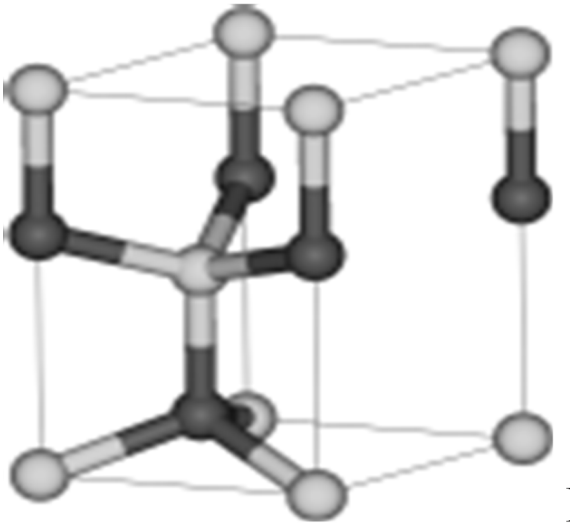

Fig. 1. Unit cell of ZnO; light grey spheres correspond to oxygen, the dark ones — to zinc [8].

Taking as perfect and absolutely pure single crystal, ZnO would be an insulator at room temperature with only 4 m^{-3} free electrons in the conduction band compared to $8 \cdot 10^{28}$ m^{-3} in metals and 10^{14}–10^{25} m^{-3} in semiconductors. The real single crystals of ZnO are found to exhibit n-type conductivity due to non-stoichiometry of the oxide. This non-stoichiometry is due to native point defects [19]. ZnO thin films were prepared from nano powders [29]. During this research work, ZnO has been studied for its doping and dependence of electrical properties on the amount of O_2 in the working gases. AZO have been grown on silicon and glass substrates using RF magnetron sputtering. These films have been grown with varying amounts of Ar and O_2 in working gases. The films showed semiconducting behaviour and a tendency towards lower activation energy (E_a). AZO thin films with the lowest required activation energy have been deposited successfully.

2. Experimental

The substrates used for the growth of AZO films were silicon and glass. The silicon substrates of 1.5 cm×1.5 cm were obtained from single crystal silicon material using a diamond pointer. The substrates were cleaned in the following procedure: after washing with deionized water, the substrates were placed in a beaker containing acetone, and the beaker was placed in an

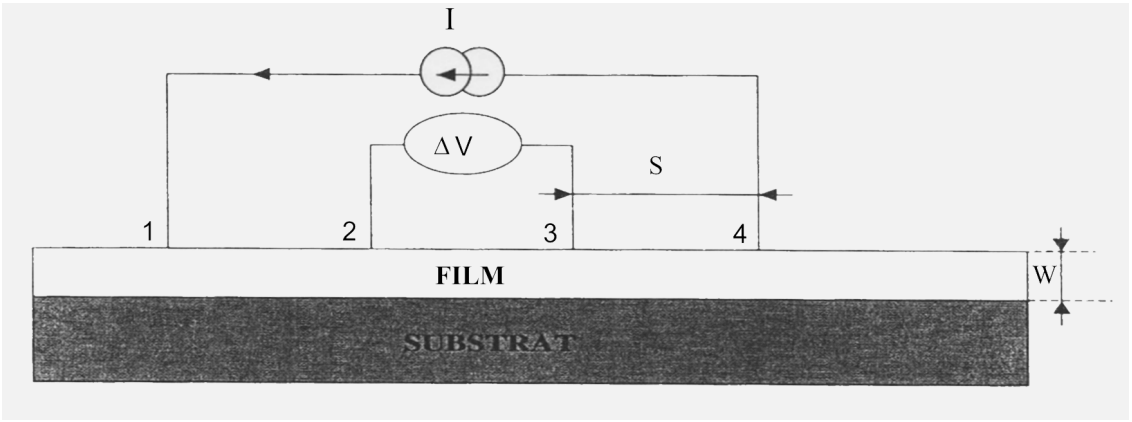

Fig. 2. Principle of operation of four-point measurements.

ultrasonic bath containing plain tap water; then the substrates were cleaned of dust and atmospheric particles by ultrasound for at least 2 minutes, washed again with deionised water and dried with nitrogen.

The glass substrates of 1.8 cm×2 cm were cut from a glass sheet and cleaned in the following procedure: washed with deionised water; put in a beaker with isopropanol, which was placed in an ultrasound bath with simple tap water; cleaned for dust, any grease and atmospheric particles with ultrasound for at least 4 minutes; washed again with deionised water and placed in a beaker with acetone for two minutes; then washed again with deionised water and dried with nitrogen.

All the films were deposited at the fixed parameters with RF of 15 MHz, a power of 100 watts, substrate temperature of 500°C, deposition pressure of 0.004 mbar. The plasma gases were Ar and O_2. For each deposition, the content of O_2 was varied between 10 %, 25 %, 50 %, and 75 % while maintaining the total concentration of 20 sccm. For the case of 75 % O_2, the total amount of working gases was 30 sccm, while the amount of O_2 was 22.5 cm^3/min and the amount of Ar was 7.5 cm^3/min.

During sputtering, atoms of the target solid material are physically knocked out into the gas phase due to bombardment of the target by energetic ions. This process is driven by the transfer of momentum due to collisions among the ions and atoms in the material. Thin films are prepared by sputtering atoms of source materials on a substrate in a vacuum chamber. Magnetron sputtering as a plasma process makes it possible to achieve higher energy inputs into growing films.

Table 1

Target material	ZnO metal disc (10 cm diameter) + Al (4 cylinders
Target-Substrate distance	6 cm
Substrates used	Silicon (1.5×1.5 cm^2) and Glass (1.8×2 cm^2)
Plasma (Ar + O_2)	20 sccm (10 %
Power	100 W
Substrate temperature	500°C
Pressure	0.004 mbar

In this work, the films were deposited using the above-mentioned technique. The chamber was first evacuated by a turbo molecular pump to a base pressure of ~ $1 \cdot 10^{-5}$ Pa. The partial pressure of the sputtering gases consisting argon and oxygen and the gas flow during the experiment was controlled by mass flow controllers. The sputtering was carried out for 2 hours and the total amount of the plasma gases was varied by changing the oxygen concentration for each sputtering. ZnO metal disc of 10 cm diameter was used as a sputtering target with four aluminium cylinders each of 2 mm diameter placed on the surface of the ZnO disc. Single crystal silicon and glass are used as the substrate materials. A pre-sputtering for 4 minutes was performed to remove any impurities or contaminations from the target surface. The substrate temperature was kept at 500°C after stabilizing the temperature value by an electronic temperature controller for 30 minutes. The parameters used for sputtering of the AZO films are given below:

Steps involved in the sputtering of the films were: attaining a working tempera-

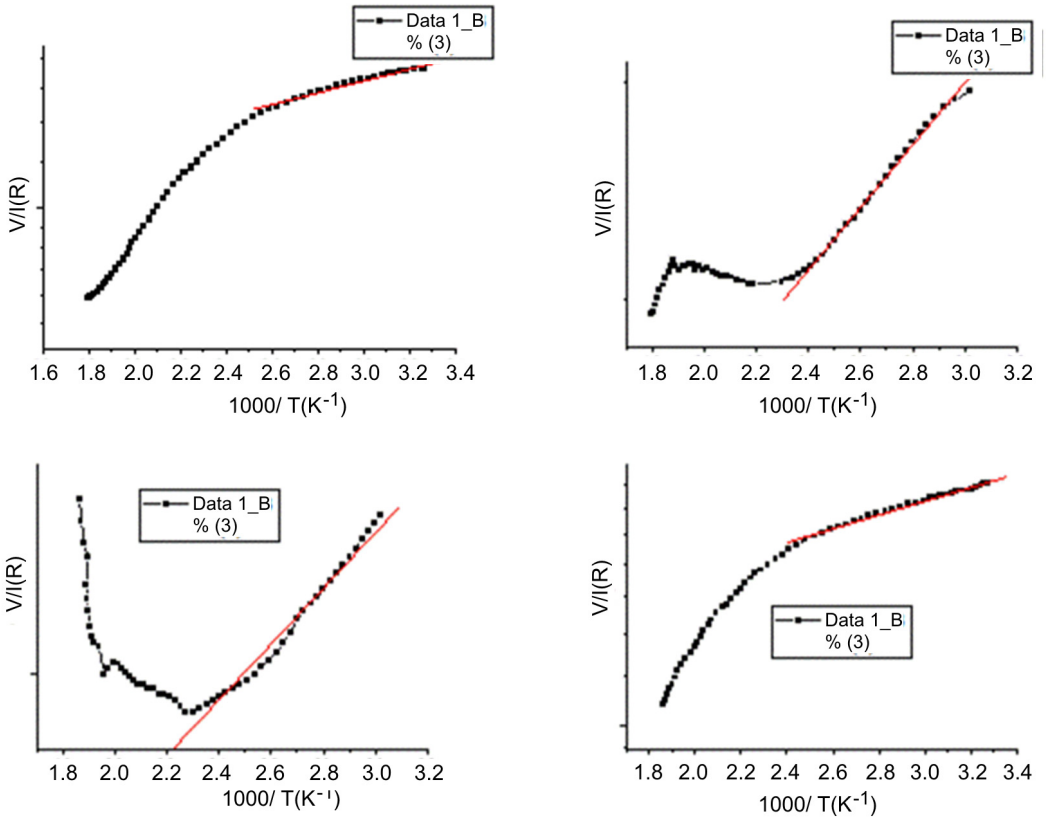

Fig. 3. A representative graph for calculation of activation energy.

ture of 500°C; achieving temperature homogenization for 30 minutes; pre-sputtering for the time of 4 minutes; sputtering of the thin films for 2 hours.

3. Results and discussion

In order to have electrical characterization for calculation of the activation energy, it was necessary to adapt the apparatus to measure resistivity and voltage/current characteristics. There are two methods used for the electrical characterization of thin films. The two point and four-point methods. The four-point method mostly used for the calculation of resistivity of semiconductors has been used in this research for the electrical characterization of the AZO thin films. The technique used also depends upon the nature of substrate utilized. The measurements are carried out depending on the temperature in steps of 10°C/min in the transition from low to high and from high to low, in the range from room temperature to 600°C.

3.1. Four point method

In this method a fixed voltage is applied between the two points 2 and 3 and the changes in the current are measured along the two points 1 and 4. The four metal points are placed on the surface of the sample, preferentially in a horizontally or flat position. The pressure of these four points over the sample surface should not be strong in order not to damage the sample surface. The resistivity (ρ) of the thin films can be calculated by the following relation:

$$\rho = \frac{2\pi S}{G\left(\frac{w}{s}\right)} \frac{\Delta v}{I}, \qquad (1)$$

where w is the thickness of the films, S is the distance between the neighboring points and $G\{w/s\}$ is the correcting factor depending upon the relation w/s and on the nature of the substrate used.

The electrical measurements are done by a system with a reading scale adjustable in height. The center of the system is constituted by four pointing knobs manufactured by the British company JANDEL. The system is a right-angled parallelepiped of dimensions 20×20×45 mm^3. The titanium points are laid out as aligned in parallel and

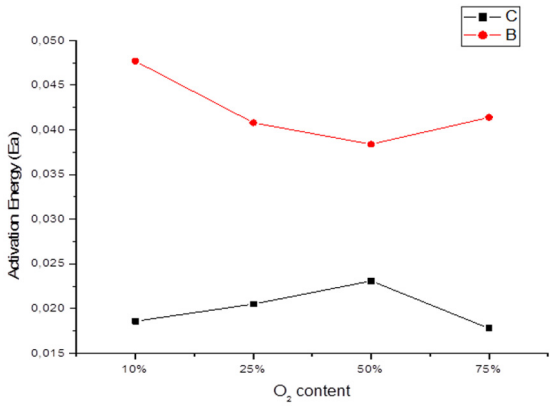

Fig. 4. Comparison between activation energy (E_a) and oxygen content with increasing and decreasing temperature. B — increasing tem-

separated by a distance of 10 mm. They are assembled on spring in order to ensure a good contact with the sample when the head is placed/descended onto the thin film. The case or cover for the four-point system is of Vitroceramic Macor, a material that is comparable to aluminum oxide in terms of electrical insulation. This is then pushed into a double cylinder of copper provided with an insulating support permitting handling of the head for reading as a whole. The only parameters directly available from the measuring equipment are voltage (V) and current (I). The other electrical quantities for the material such as resistivity, conductivity, current density, activation energy and electric field, etc. could be calculated from the voltage and current using appropriate relations. The acquired films were characterized for electrical behaviour by the four-point method, and activation energy (E_a) of the AZO thin films was calculated. (The obtained data and their plot along with equation for calculation of activation energy is attached in data files). Activation energy (E_a) was calculated from the slopes of plots according to the following relations:

$$Y = A + B(X),$$
$$\ln(V/I) = A + B(1000/T_K),$$

where $B \cdot 1000 = E_a/2K$, where K is the Boltzmann constant, $8.617 \cdot 10^{1965}$ eV/K,

$$E_a = 2K \cdot B \cdot 1000eV.$$

The most common defects in ZnO are oxygen and zinc vacancies. Oxygen vacancies (V_o) have lower formation energies than the zinc interstitials (Zn_i) and are therefore

Table 2

Group	Element	E_a, eV
Group I	Li	0.09
	Na	0.17
	K	0.32
Group III	Al	−0.03
Group V	N	0.40
	P	0.93
	As	1.15

more abundant under Zn-rich conditions. Under O_2-rich conditions, Zn vacancies (V_{Zn}) dominate [30]. It is also observed that oxygen and Zn vacancies act as residual donor impurities and native point defects in ZnO [31]. Therefore, intrinsic (un-doped) ZnO possesses n-type conductivity due to these native point defects. The conductivity of ZnO could further be enhanced by extrinsic doping with group-III elements such as Al [32]. In AZO thin films, Al enhances semiconducting behaviour of the ZnO by making efficient donors. However, the role of simplest and native point defects such as Zn and O vacancies is also very important in forming the overall n-type character of AZO films. Rapid defect annihilations take place at temperatures higher than 150 K [33]. It is observed that in the case of excess of oxygen atoms in the film, interstitial or grain boundary oxygen atoms trap free electrons [34]. The resistivity of the films has been observed to increase steeply with an increase in oxygen partial pressures. It has also been demonstrated that ZnO films deposited by reactive sputtering of a Zn target in O2/Ar atmosphere produces n-type ZnO at low O_2/Ar ratios and moderately p-type ZnO at higher O_2/Ar ratios. Whereas a fractional composition of 50 % oxygen produced n-type ZnO, a composition of 83 % oxygen produced p-type ZnO [32].

From calculation of the activation energies (E_a) for various oxygen contents and with increasing and decreasing temperatures, it could be concluded that oxygen can easily penetrate into growing films and capture free carriers, which leads to a decrease in conductivity. According to the results of the present work, oxygen does not have a pronounced effect on the conductivity of the films up to 50 % in the working gas, but after increasing its content to 75 % in the working gas, it has a strong effect. At this amount oxygen atoms act as carrier traps and reduce the conductivity even at

increasing temperature. The behaviour of the films during decreasing temperature confirms the semiconductor behaviour of the AZO films. Activation energy value for AZO films has not been reported until now. However, E_a of ZnO with some other elements have been calculated [5] and presented here for a comparison.

4. Conclusions

Characterization results obtained and their analysis confirm the presence of all the elements Zn, Al and O_2 in the films. AZO thin films showed semiconductor behaviour. Oxygen behaves as a donor up to 50 % in the working gas ($Ar + O_2$). As the oxygen content increases to 75 % in the working gases, it acts as a carrier trap and thin films have higher activation energy.

Acknowledgment.

Dr. Laurent Lebrizoula and Dr. Sarry Frederic are greatly acknowledged for their supervision and support in carrying out the experimental work. The experimental work was done at Laboratory for the Physics of Ionized Media and Applications (LPMIA), University Henri Poincare, Nancy, France. There is no conflict of interest on the part of author.

References

1. U.Ozgur, D.Hofstetter, H.Morkoc, *Proceedings of IEEE*, **98**, 1255 (2010).
2. Xinglai Zhang, Jing Li, Wenjin Yang et al., *ACS Appl. Mater. Interfaces*, **11**, 24459 (2019).
3. Junqing Zhao, Shijie Xie, Shenghao Han et al., *Synthetic Metals*, **114**, 251 (2000).
4. A.R.Gentle, S.D.Yambem, P.L.Burn et al., *J. Applied Physics*, **119**, 245501 (2016).
5. U.Ozgur, Ya.I.Alivov, C.Liu et al., *J. Applied Physics*, **98**, 041301 (2005).
6. Hasan Eskalen, Yusuf Kavun, Suleyman Kerli et al., *Optical Materials*, **105**, 109871 (2020).
7. Yajing Liu, Qingyu Hou, Shulin Sha et al., *Vacuum*, **17**, 109127 (2020).
8. C.Klingshirn, *Chem. Phys. Chem.*, **8**, 782 (2007).
9. B.Kucukgok, B.Wang, A.G.Melton et al., *Phys. Status Solidi C*, **11**, 894 (2014).
10. M.Husham, Mohd Nizar Hamidon, S.Paiman et al., *Sensors and Actuators A* **263**, 166 (2017).
11. Ying-Jie Lu, Zhi-Feng Shi, Chong-Xin Shan et al., *Chin. Phys. B*, **26**, 047703 (2017).
12. Yangyang Zhao, Yicong Chen, Guofu Zhang et al., *Nanomaterials*, **11**, 240 (2021).
13. Sara Marouf, Abdelkrim Beniaiche, Kasra Kardarian et al., *J. Anal. Appl. Pyrolysis*, **127**, 299 (2017).
14. Sana Ullah, Fabio De Matteis, Ivan Davoli, *J. Electronic Materials*, **46**, 6609 (2017).
15. Sana Ullah, Rita Branquinho, Ana Santa et al., *Semicond. Sci. Technol.*, **33**, 105004 (2018).
16. J.C.A.Queiroz, M.Naeem, J.B.A.Filho, M.S. et al., *J. Electronic Materials*, **50**, 687 (2021).
17. Sana Ullah, Rita Branquinho, Tiago Mateus et al., *Sustainability*, **12**, 10423 (2020).
18. H.T.Cao, C.Sun, Z.L.Pei et al., *J. Materials Science: Materials in Electronics*, **15**, 169 (2004).
19. Wolfgang H. Hirschwald, *Acc. Chem. Res.*, **18**, 228 (1985).
20. R.M.Pshenychnyi, O.V.Lysenko, T.V.Pavlenko et al., *Functional Materials*, **30**, 18 (2023).
21. A.C.Badgujar, Brijesh Singh Yadav, Golu Kumar Jha et al., *ACS Omega*, **7**, 14203 (2022).
22. Yupeng Xie, Xinhai Li, XianDe Wang, *Functional Materials*, **27**, 337 (2020).
23. Eugen Stamate, *Surface & Coatings Technology*, **402**, 126306 (2020).
24. Naveen Kumar, Ashraful Haider Chowdhury, Behzad Bahrami et al., *Thin Solid Films*, **700**, 137916 (2020).
25. Eugen Stamate, *Nanomaterials*, **10**, 14 (2020).
26. Le Kong, Jinxiang Deng, Liang Chen et al., *Functional Materials*, **24**, 541 (2017).
27. T.O.Berestok, D.I.Kurbatov, N.M.Opanasyuk et al., *Functional Materials*, **22**, 93 (2015).
28. E.I.Getman, T.M.Savankova, A.V.Ignatov et al., *Functional Materials*, **21**, 247 (2014).
29. R.S.Khaleel, M.Sh.Hashim, S.Gh.Majeed, *Journal of Science*, **49**, 1 (2022).
30. A.F.Kohan, G.Ceder, D.Morgan et al., *Physical Review*, **61**, 15019 (2000).
31. S.Tuzemen, Gang Xiong, John Wilkinson et al., *Physics B*, **308–310**, 1197 (2001).
32. D.C.Look, C.Coskun, B.Claflin et al., *Physica B*, **340–342**, 32 (2003).
33. Takashi Tsuji, Mitsuji Hirohashi, *Applied Surface Science*, **157**, 47 (2000).
34. Yasuhiro Igasaki, Michiaki Ishikawa, Goro Shimaoka, *Applied Surface Science*, **33–34**, 926 (1988).