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Effect of Oxygen Pressure on the Structural, Morphology and Optical Properties of Nanocrystalline TiO_2 Thin Films Prepared by Pulsed Laser Deposition

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Abstract

Nonstructural TiO_2 thin films were prepared by Pulsed Laser Deposition (PLD) on the SiO_2 substrates at a variable pressure of oxygen (0.01, 0.1, 10) mbar and higher substrate temperature (Ts = 400 °C) . The crystal structure was determined by using X-ray diffraction (XRD). The XRD pattern shows the an increase in the average size of the crystalline grains various for R(110) from (82.2 nm) to (164.4 nm) and shift the films to be amorphous by increase Oxygen pressure. The morphology properties were determined from Scan Electron Microscopy (SEM).The formation of pours has also been studied using Atomic Force Microscopy (AFM). The SEM and AFM images reveal uniform distributions of grains in the films and grains are in the Nanocrystalline dimensions. Optical properties were investigated by obtaining the transmittance spectrums in the UV-Visible regions as a function of wavelength. Transmittance results is upper than ~80% which makes these films suitable for sensor applications.

Keywords: Pulsed Laser Deposition (PLD), TiO_2-SiO_2 Thin Films

1. Introduction

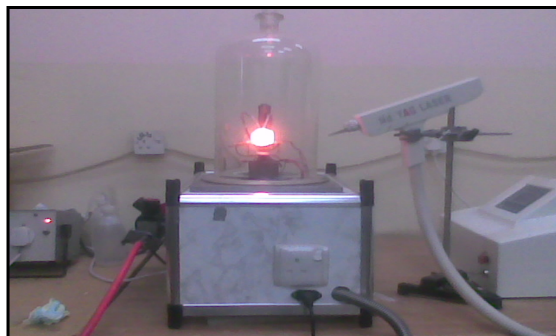
Titanium dioxide is a wide band semiconductor which exists in three crystallographic phases: rutile, anatase and brookite. The first two polymorphs have a tetragonal symmetry and due to their strong photocatalytic properties and stability have become materials of high scientific interest. TiO_2 nanostructures, as they significantly reinforce the photocatalytic properties of titanium, are commonly used in optical devices (S.H. Jeong et al., 2004), self-cleaning protective coatings (Z. Jiwei et al., 1999), sensors (K.M. Chen et al., 1999), etc. TiO_2 nanocrystals, most often doped with organic dyes or metals in order to shift their absorbance to the visible light region, are widely used in solar cells as effective energy converters (C. Byun et al. , 1997 ; D. Mardare and P. Hones , 1999) . The anatase phase is especially adequate for those applications due to its crystal structure and a higher band gap of

3.2 eV compared to the 3 eV in rutile (T. Modes et al., 2005; M. Zhang, 2007). However H. Kawasaki et al. (2000) and H.long et al. (2008) have revealed that for some photocatalytic processes, the combination of anatase and rutile is optimum. Pulsed laser deposition (PLD) is considered as a flexible method for obtaining well defined nanostructures and surface morphologies (Z. Zhao et al., 2004; Y.Yang et al. 2009). Changing the deposition parameters allows one to tune the properties of deposits according to the application. Several studies on UV laser deposition of TiO_2 (S.M.Sze, 2007) have explored the influence of substrate temperature, inlet gas pressure and/or laser wavelength, pulse duration and fluence, trying to control the quality of grown deposits. However some aspects of the growth of titania nanostructures by PLD remain under intense scientific discussion , particularly the deposition conditions for obtaining a pure phase anatase or rutile films (C.D. Wagner et al. , 1981 ; J.F. Marco et al. , 2005 ; M. Walczak et al. , 2008) .

2. Experimental

The deposition was carried out using a Q switched Nd:YAG laser with a frequency second radiation at 532 nm (pulse width 10 ns repetition rate 6 HZ) and fluencies energy 0.8 J/cm^2 . TiO_2 films were grown by pulsed laser deposition on optically flat glass substrates kept an on-axis distance of 5 cm from the TiO_2 target, as shown in Fig.1. The TiO_2 pellet was ablated from 30-50 pulses (5-10) min to get single layered thin films. During the deposition the Oxygen pressure was kept at (0.01 , 0.1 , 10) mbar respectively. XRD measurements (Philips PW 1050, λ=1.54 Å) measurements using Cu kα shows crystalline structure of the films. Spectra of all the films were recorded using a UV-ViS (Perkin Elemer Company) spectrophotometer , In the sp the chamber was kept at vacuum pressure of ectral range of (200-900) nm. Transmission measurements were performed for a range (400-900) nm using UV-VIS-PV-8800 (Perkin Elemer Company) spectrophotometer. The characterizations included determination of the absorption coefficient as a function of incident photon energy, determination the value energy gap. The surface morphology was examined by scanning electron microscopy (SEM–JEOL 7000) and by atomic force microscopy (AFM-Digital Instruments NanoScope) working in tapping mode. Typical film thickness was 200 nm, as measured by Laser (He-Ne).

Figure 1: Experimental Setup.



3. Result and Discussion

3.1. Structural Properties

Fig.2 presents the XRD patterns of TiO_2 thin films of 200 nm thickness, deposited at different Oxygen pressure. from Fig.2.a at Oxygen pressure 0.001 mbar we have shown the most stable structure of the membrane phase of TiO_2 and Rutile at the levels (110) and (200) at $2\theta=30^o$ and $2\theta=44^o$ respectively . At Fig.2.b we have shown levels of new crystal belongs to the less stable phase Anatase for tow levels

(101) and (004) at 2θ= 25.4° and 2θ=39° respectively, in addition to the level R(110) at 2θ=30° at Oxygen pressure 0.1 mbar.

The reason is that the length of bound Ti-O in phase Rutile Longer ones in the process of phase Anatase (S. Eliezer et al. , 2004) , This means that the energy of band Ti-O in Rutile smaller than band in Anatase. Therefore, the formation of membrane phase Rutile molecules need to possess a high kinetic energy of any pressure less oxygen because increasing the oxygen pressure increases from the collision between particles and thus reduces the kinetic energy and is identical to the findings of the researcher J.N.Zeng et al. (2002).

Also, the reduced oxygen pressure leads to left voids in the membrane formed with high kinetic energy of molecules vaporized. That the increased pressure of oxygen will reduce these gaps and thus diminished levels of crystalline and turns to the installation of the membrane structure of amorphous, because of the plasma from reaching the ground glass and this is what we observe as Fig.2.c.

Having also examined the effect of oxygen pressure on the rate of grain size as shown in the table 1 .

Figure 2: The XRD of TiO_2 Thin Films: (a) 0.01 mbar, (b) 0.1 mbar, (c) 10 mbar.

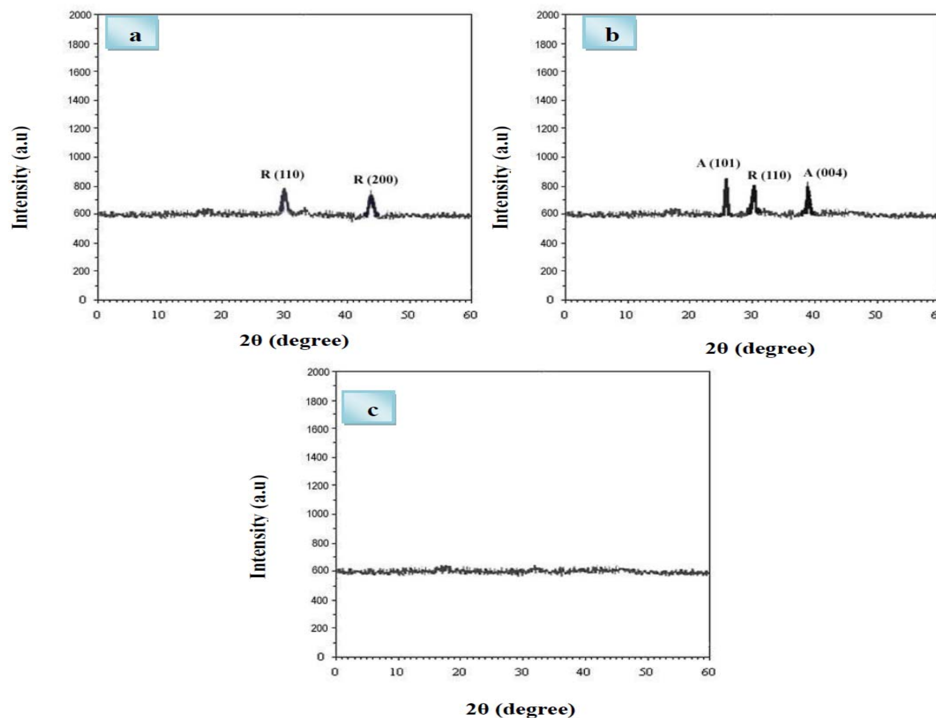


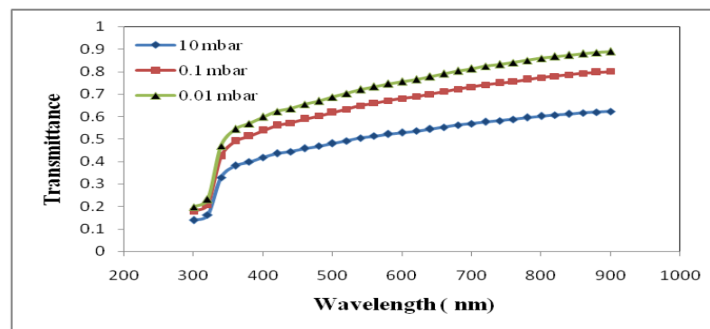
Table 1: The XRD Patterns of TiO_2 Thin Films Deposited at Different Oxygen Pressure.

Grain size (nm)	FWHM°	(hkl)	2θ (degree)	O_2 pressure (mbar)
82.22	0.1	R(110)	30	0.01
68.5	0.125	R(200)	44	
81.41	0.05	A(101)	25.4	0.1
164.4	0.05	R(110)	30	
93.6	0.09	A(004)	39	
-	-	-	-	10

3.2. Optical Properties

Fig.3. shows transmittance spectra as a function of the wavelength of the change over between (300-900) nm of the TiO_2 film grown at (0.01, 0.1, 10) mbar with Ts = 400 °C and fluencies energy 0.8 J/cm^2 . The average transmittance of TiO_2 films is over 80% . Where we note that transmittance spectra for film grown at 10 mbar is less than the transmittance at a pressure of oxygen 0.1 mbar . This, in turn, at a pressure of less 0.01 mbar , Indicating that the increased pressure of Oxygen leading to increased surface roughness of the membrane and the membrane formed into amorphous at a pressure of 10 mbar , This is also indicated by XRD tests . We also note when the pressure is getting low Oxygen transmittance due to irregular distribution of optical granular and accompanied by a decrease in the scattering of light.

Figure 3: Transmittance spectra of TiO_2 Thin Films Deposited at Different Oxygen Pressure.



In order to determine the value of energy gap as well as the dominant absorption processes in such material, the relation of $(\alpha h\nu)^2$ with the incident photon energy (hν) is explained in Fig. (4). The obtained value of energy gap is about 3.7 eV and it is very close to the value obtained by previous works (Z. Zhao et al. , 2004; H.Long et al.,2008) . The relation was linear, which indicates that the TiO_2 of this work has direct energy gap. And the direct allowed absorption processes are the dominant the energy gap increases with decreases Oxygen pressure The absorption coefficient (α) of such processes is given by (S.M.Sze ,2007) :

$$\alpha = A(h\nu - E_g)^n$$

Where α is absorption coefficient and n =1/2 for direct transition where A is a parameter independent of hν and Eg is the optical band gap energy. Plotting the dependence of $(\alpha h\nu)^2$ vs. hν, the value of Eg can be determined by extrapolating the linear portion of this plot to $(\alpha h\nu)^2 = 0$.

Having also examined the effect of oxygen pressure on the rate of energy gab as shown in the table 2 .

Figure 4: The Relation Between $(\alpha h\nu)^2$ And hν For TiO_2 Thin Films Deposited at Different Oxygen Pressure.

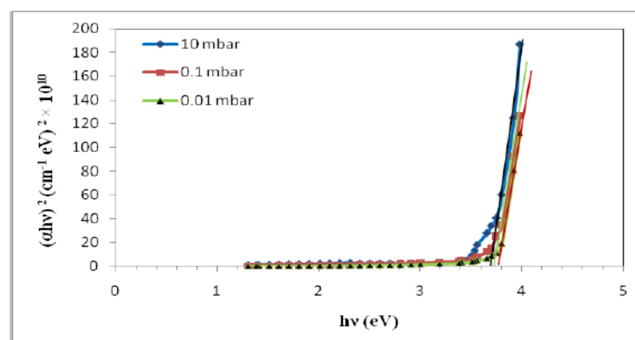


Table 2: The Value of Energy Gab For TiO_2 Thin Films Deposited at Different Oxygen Pressure.

Energy Gab (eV)	Thin Film
3.79	TiO_2 at Oxygen Pressure 0.01 mbar with Ts = 400 °C and fluencies energy 0.8 J/cm^2 .
3.72	TiO_2 at Oxygen Pressure 0. 1 mbar with Ts = 400 °C and fluencies energy 0.8 J/cm^2 .
3.7	TiO_2 at Oxygen Pressure 10 mbar with Ts = 400 °C and fluencies energy 0.8 J/cm^2 .

3.3. Morphology Properties

Fig. 5 presents SEM images of the surface of deposits grown at various Oxygen pressure (0.01, 0.1, 10) mbar at a constant Ts = 400 °C and fluencies energy 0.8 J/cm^2 . We find from the Figure that the morphology of the surface change depending on the Oxygen pressure at the deposition of prepared film, as the increasing pressure of oxygen lead to increased grain size and an increase in the density of particles deposited. The mechanism of formation of particles is described as follows: After the proliferation of free molecules on the surface of the ground, the average free path of molecules decrease the presence of oxygen, because the high pressure O_2 Increases the collisions between molecules leads to the loss of energy particles in an amount sufficient for the formation of molecular clusters, these clusters reach the surface of the base granules are small and then start to grow to form what is known as the islands (J. N. Zeng et al. ,2002).

Figure 5: The SEM Image of TiO_2 Thin Films: (a) 0.01 mbar, (b) 0.1 mbar, (c) 10 mbar.

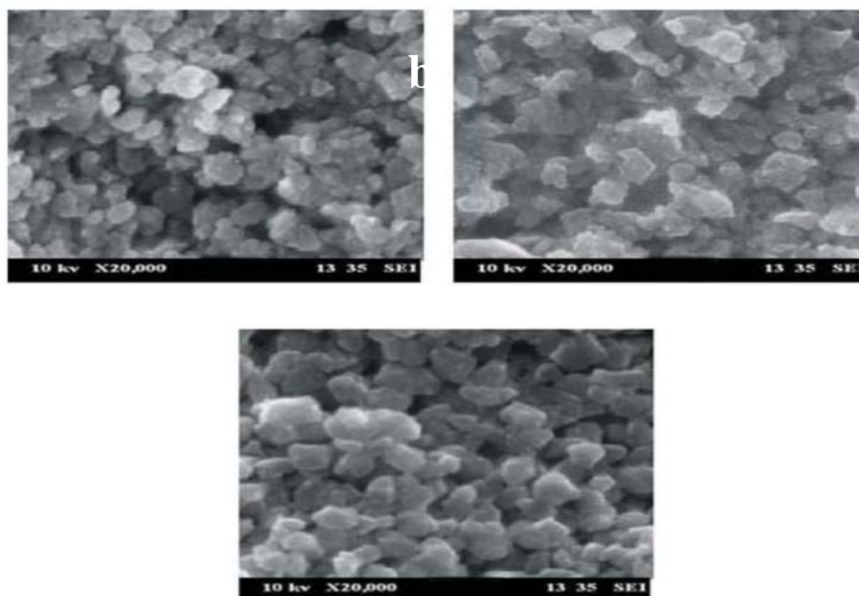


Fig.6 AFM topography images shows that the increase of oxygen pressure, we note an increase in surface roughness, reaching (4,6) nm at pressure (0.01 , 0.1) mbar respectively . Also, the increasing pressure of oxygen shows a homogeneous distribution of the nanoparticles as a result of an interaction between the molecules Ti and gas O_2 resulting nano-particles containing both Ti and O_2. We also note

also that the increased pressure of oxygen leading to increased surface roughness of the film as shown in table 3, and our results agree with the findings of the researcher (Yoshiaki Suda et al., 2004).

Figure 6: The AFM Image of TiO_2 Thin Films: (a) 0.01 mbar, (b) 0.1 mbar, (c) 10 mbar.

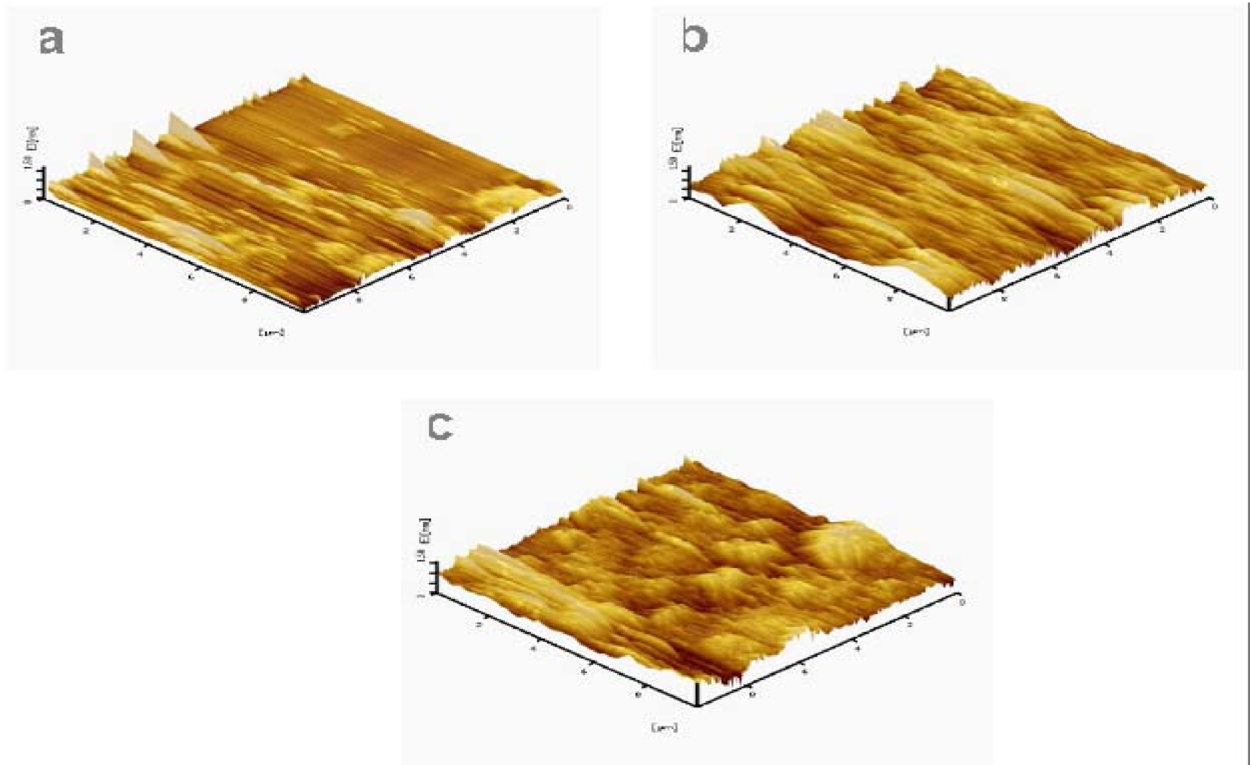


Table 3: The Value of Grain Size and Roughness For TiO_2 Thin Films Deposited at Different Oxygen Pressure.

Roughness RMS(nm)	Grain size AFM (nm)	Grain size SEM (nm)	Grain size XRD (nm)	Sample
4	80.4	80	82.22	TiO_2 at Oxygen pressure (0.01 mbar)
6	82	83	81.41	TiO_2 at Oxygen pressure (0.1 mbar)
8.3	- c	-	-	TiO_2 at Oxygen pressure (10 mbar)

4. Conclusions

TiO_2 thin films as they are prepared using the PLD method, the structural of the films were analysis shows the film has polycrystalline and amorphous structure sometimes depending on preparation conditions. The energy band gap was found 3.7 eV. Roughness of material surface increased with increasing Oxygen pressure.

References

[1] S.H. Jeong , J.K. Kim, B.S. Kim , S.H. Shim , B.T. Lee ,2004." Determination of photocatalytic activity in amorphous and crystalline titanium oxide films prepared using plasma-enhanced chemical vapor deposition", Applied Surface Science , Lett. 76, p.507.

[2] Z. Jiwei , Y. Tao, Z. Liangying , Y. Xi ,1999." Atomic layer deposited titanium dioxide and its application in resonant waveguide grating", Ceram. Int. Lett.25 , p.667.

[3] K.M. Chen, A.W. Sparks, H.C. Luan, D.R. Lim, K.Wada, L.C. Kimerling ,1999." Si-based omnidirectional reflector and transmission filter optimized at a wavelength of 1.55 μm", Appl. Phys. Lett. 75 , p. 3805.

[4] C. Byun, Y. Kim, W.J. Lee, B.W. Lee,1997." Characteristics of Metal/Ferroelectric/Insulator/Semiconductor Using La2O3 Thin Film as an Insulator", Jpn. J. Appl. Phys. Lett.36, p. 5588.

[5] D. Mardare, P. Hones, Mater,1999." Development of microfabricated TiO2 channel waveguides", Sci. Eng. Lett.68, p. 42.

[6] T. Modes, B. Scheffel, C. Metzner, O. Zywitzki, 2005." High-rate low-temperature dc pulsed magnetron sputtering of photocatalytic TiO2films: the effect of repetition frequency", E. Reinhold, Surf. Coat. Technol. Lett. 200 , p. 306.

[7] M. Zhang, G. Lin, C. Dong, L.Wen ,2007." Crystal Structure of TiO_2 Thin Films grown on Sapphire Substrates by RF Sputtering as a Function of Temperature", Surf. Coat. Technol. Lett. 201 , p. 7252.

[8] H. Kawasaki, K. Doi , S.Hiraishi , Y.Suda , 2000." Grain-Orientation Induced Work Function Variation in Nanoscale Metal-Gate Transistors—Part II: Implications for Process, Device, and Circuit Design", Jpn.J. Appl. Phys. Lett.39, p. 4525.

[9] H.long, G.Yang, A.Chen Y.Li, P. Lu , 2008." A project to encourage collaborative research and innovation between Canadian and Chinese research groups", thin films Lett.517, pp. 745-749.

[10] Z. Zhao, B.K. Tay, G. Yu,2004." Room-Temperature Deposition of Amorphous Titanium Dioxide Thin Film with High Refractive Index by a Filtered Cathodic Vacuum Arc Technique", Appl. Opt. Lett.43, p. 1281.

[11] Y.Yang, H.Wang, X.Li, C.Wang , 2009." Crystalline-Amorphous Core-Shell Silicon Nanowires for High Capacity and High Current Battery Electrodes", materials letters Lett.63, pp.331-333.

[12] S.M.Sze, 2007." physics of semiconductor device", 3rd edition, john wiley.

[13] C.D. Wagner, L.E. Davis, M.V. Zeller, J.A. Taylor, R.M. Raymond, L.H. Gale ,1981, Surf. Interface Anal. Lett.3 , p. 211.

[14] J.F. Marco, A. Cuesta, M. Gracia, J.R. Gancedo, P. Panjan, D. Hanzel, 2005. Thin Solid Films Lett.492, p. 158.

[15] M. Walczak, M. Oujja, M. Sanz, J.F. Marco, M. Castillejo, 2008. Appl. Phys. A , doi:10.1007/s00339-008-4704-y.

[16] S. Eliezer , N. Eliaz , E. Grossman , D. Fisher , I. Gouzman , Z. Henis , S. Pecker , Y. Horovitz and M. Fraenke ,2004."Synthesis of Nanoparticles with Femtosecond Laser Pulses", Phys. Rev. B 69, p.14119.

[17] J. N. Zeng , J. K. Low , Z. M. Ren , T. Liew and Y. F. Lu ,2002. "Effect of Deposition Condition on Optical and Electrical Properties of TiO_2 Films Prepared by Pulsed Laser Deposition", Appl. Sur. Sci. ,Vol. 197-198, p.362.

[18] Yoshiaki Suda, Hiroharu Kawasaki, Tamico Ohshima and Tsuyoshi Ueda , 2004." Characterization of TiO_2 Thin Films as A photocatalytic Prepared Using the Pulsed Laser Deposition Method", Phys. Stat. Sol. (c) ,Vol. 3 , p.1250.