TiO_2 nanofilm growth by Ti ion implantation and thermal annealing in O_2 atmosphere postprint

Authors: ZHOU Xiaodong, ZHOU Si-Hua, SUN Xian-Ke, ZHANG Yun-Li

Date: 2023-06-18T00:00:00+00:00

Abstract

TiO2 nanofilms on surface of fused silica were fabricated by Ti ion implantation and subsequent thermal annealing in oxygen ambience. The silica glasses were implanted by 20 kV Ti ions to 1.5$×$10^{17} ions/cm2 on an implanter of metal vapor vacuum arc (MEVVA) ion source. Effects of annealing parameters on formation, growth and phase transformation of the TiO2 nanofilms were studied in detail. Optical absorption spectroscopy, Raman scattering spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy and transmission electron microscopy measurements were done to figure out formation mechanism of the TiO2 nanofilms. The formation of TiO2 nanofilms was due to out-diffusion of the implanted Ti ions to the substrate surface, where they were oxidized into TiO2 nanoparticles. Formation, phase, and thickness of the TiO2 nanofilms can be well tailored by controlling annealing parameters.

Full Text

Preamble

TiO2 Nanofilm Growth by Ti Ion Implantation and Thermal Annealing in O2 Atmosphere

ZHOU Xiao-Dong, ZHOU Si-Hua, SUN Xian-Ke, and ZHANG Yun-Li
School of Physics and Electromechanical Engineering, Zhoukou Normal University, Zhoukou 466001, China

(Received March 13, 2015; accepted in revised form April 19, 2015; published online June 20, 2015)

TiO2 nanofilms on the surface of fused silica were fabricated by Ti ion implantation and subsequent thermal annealing in oxygen atmosphere. The silica glasses were implanted with 20 kV Ti ions to a fluence of 1.5 × 10^{17} ions/cm^2 using

a metal vapor vacuum arc (MEVVA) ion source implanter. The effects of annealing parameters on the formation, growth, and phase transformation of the TiO2 nanofilms were studied in detail. Optical absorption spectroscopy, Raman scattering spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, and transmission electron microscopy measurements were performed to elucidate the formation mechanism of the TiO2 nanofilms.

The formation of TiO2 nanofilms resulted from the out-diffusion of implanted Ti ions to the substrate surface, where they were oxidized into TiO2 nanoparticles. The formation, phase, and thickness of the TiO2 nanofilms can be well tailored by controlling the annealing parameters.

Keywords: Ion implantation, Thermal annealing, TiO2 nanofilms, Characterization
DOI: 10.13538/j.1001-8042/nst.26.030507

Introduction

Since Honda and Fujishima reported TiO2-photoassisted electrochemical water splitting in 1972 [1], titanium oxides have attracted significant attention due to their wide applications in photocatalysis for environmental treatment and hydrogen production, dye-sensitized solar cells for photovoltaics, sensors, smart windows, and display devices [2–5]. Conventional TiO2 powder catalysts suffer from disadvantages requiring stirring during reaction and separation after reaction. TiO2 thin films overcome these limitations and enable broader industrial applications. Various techniques have been employed to prepare TiO2 thin films, including sol-gel processing [6], spray pyrolysis [7, 8], magnetron sputtering [9], and chemical vapor deposition [10].

Photocatalytic TiO2 films prepared by wet chemistry processes (e.g., sol-gel method) exhibit good photocatalytic performance, but their mechanical durability is insufficient for practical applications such as self-cleaning glasses for windows and automotive mirrors. Additionally, they are generally inferior for applications requiring large-area films [11]. While these TiO2 films face limitations due to unsatisfactory stability and reliability, TiO2 films fabricated by physical methods generally exhibit higher film adhesion and stability for practical use [12].

Nanomaterials, nanoparticles, and nanofilms can be fabricated by ion implantation. Metal oxide semiconductors are produced through a solid-phase growth process involving metal ion implantation and subsequent thermal oxidation, such as ZnO [13–16] or TiO2 [17, 18] nanomaterials via Zn or Ti ion implantation. Nanofilms fabricated by ion implantation, due to their formation at high temperatures, typically demonstrate good adhesion and stability. In this paper, TiO2 nanofilms were formed on fused silica substrates through a solid-phase growth process of Ti ion implantation and subsequent thermal annealing in oxygen atmosphere. The effects of implantation and annealing parameters on the formation, phase, and growth of the TiO2 nanofilms were investigated to under-

stand the mechanisms of TiO2 nanofilm formation. The nanofilm thickness and phase can be effectively tailored by controlling the implantation and annealing parameters.

Experimental

Sample Preparation

High-purity silica slides (20 mm × 20 mm × 1 mm) were implanted with 20 kV Ti ions to a fluence of 1.5 × 10^{17} ions/cm^2 using a metal vapor vacuum arc (MEVVA) ion source implanter. The samples were continuously rotated in a horizontal plane during ion implantation, with the sample holder cooled by circulating water. The implanted samples were annealed under O2 atmosphere in a conventional tube furnace. Group 1 samples were annealed for 2 h at 500 °C, 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C. Group 2 samples were annealed at 800 °C for 2, 4, and 6 h.

Sample Characterization

Optical absorption spectra of the samples were measured using a UV-vis-NIR dual-beam spectrophotometer (Varian Cary5000) in the wavelength range of 200–800 nm. Surface morphologies of the implanted samples before and after thermal annealing were examined using scanning electron microscopy (SEM, FEI Sirion). Raman scattering spectra were measured using a micro-Raman microscope (Jobin-Yvon LabRAM HR) equipped with a cooled CCD detector in backscattering geometry to identify the crystalline phase of TiO2. The excitation source was the blue line (488 nm) of an Ar+ laser operated at 5 mW, with scan density varying from 100 to 1200 cm^−1. Microstructural characterization of the as-implanted and annealed samples was performed using a JEOL 2010 (HT) transmission electron microscope (TEM) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a Kratos XSAM800 XPS system with Mg Kα (1253.6 eV) radiation under a vacuum of 6 × 10^−7 Pa.

Results and Discussion

Optical Absorption Spectra of Ti-Implanted Samples Versus Annealing Temperature

Figure 1 [Figure 1: see original paper] shows the optical absorption spectra of the as-implanted sample and samples annealed for 2 h at 500–1000 °C. The absorption spectrum of the as-implanted sample exhibits a drastic increase in background absorption in the UV and visible regions, attributed to absorption by implantation-induced point defects and Ti nanoparticles formed in the silica substrate. After annealing at 500 °C, the background absorption decreases significantly due to defect annihilation by thermal annealing. Additionally, an abrupt absorption edge appears, indicating the presence of anatase TiO2 [19, 20]

formed during post-implantation annealing at 500 °C. For all annealed samples, the spectra show a trend where the absorption edges shift to longer wavelengths with increasing annealing temperature, implying an increase in the mean size of TiO2 nanoparticles.

Notably, the sample annealed at 1000 °C differs markedly from other annealed samples, exhibiting a greater shift of the absorption edge to longer wavelengths. This remarkable shift suggests that phase transformation of TiO2 from anatase to rutile may occur at 1000 °C. Such shifts in the maximum absorption and absorption edge induced by phase transformation are consistent with results reported in Refs. [20, 21].

SEM Images of Ti-Implanted Samples Versus Annealing Temperature

Surface morphologies of the samples were investigated by SEM. Figure 2 [Figure 2: see original paper] shows SEM images of Ti-implanted samples annealed for 2 h at 500, 600, 700, 800, 900, and 1000 °C. Overall, the surface morphology changes significantly for samples annealed at different temperatures. At 500 °C, small nanoparticles begin to appear, indicating TiO2 nanoparticle formation. At 600 °C, a smooth and homogeneous film forms, with numerous near-spherical nanoparticles distributed compactly on the substrate surface. The TiO2 nanoparticle sizes increase with annealing temperature, with mean diameters of 25.3 nm, 37.6 nm, and 45.8 nm at 600 °C, 700 °C, and 800 °C, respectively. At 900 °C, however, the TiO2 nanoparticles on the surface aggregate and form cross-linked particles approximately 61.4 nm in diameter. The surface morphology undergoes a substantial change at 1000 °C, with TiO2 nanoparticles in the substrate surface becoming embedded and indistinguishable.

The evolution of surface morphologies as a function of annealing temperature in Figure 2 correlates well with the optical absorption spectra results (Figure 1). The increase in both particle size and crystal quality as a function of annealing temperature leads to the absorption edge shifting toward longer wavelengths. The abrupt shift of the absorption edge observed at 1000 °C corresponds to the structural change characterized by SEM, likely resulting from the phase transformation from anatase to rutile.

Formation and Phase of TiO2 Nanocrystals: Raman Scattering Spectroscopy and XPS Measurements

Raman spectroscopy measurements were performed to identify and analyze the formation and phase of TiO2 nanocrystals after thermal annealing. Figure 3 [Figure 3: see original paper] shows Raman spectra of bare silica, the as-implanted sample, and Ti-implanted samples annealed for 2 h at 500–1000 °C. Some Raman peaks of SiO2 are observed in the bare silica sample. However, the Raman spectrum of the as-implanted silica becomes almost featureless due to extensive structural damage induced by ion implantation. The silica structure is partially recovered by subsequent thermal annealing, and the Raman peaks

of SiO2 reappear in the annealed samples. A Raman peak centered at approximately 140 cm^−1 appears at 600 °C, which can be assigned to the Eg mode of TiO2 in the anatase phase [22, 23]. The Raman peak intensity increases with temperature from 600 °C to 900 °C, indicating increased crystallinity and amount of the anatase-phase TiO2. However, for the sample annealed at 1000 °C, the spectrum shape changes, showing three Raman peaks centered at 605, 440, and 230 cm^−1, which can be ascribed to two-phonon scattering of A1g and Eg modes and the second-order effect of the rutile-phase TiO2, respectively [24]. Thus, the anatase-to-rutile phase transformation at high temperature is confirmed.

The formation and evolution of the anatase phase in the annealed samples is consistent with the evolution of optical absorption spectra in Figure 1 and SEM images in Figure 2. The increase in nanoparticle size and crystal quality as a function of annealing temperature leads to the red-shift of the absorption edge and intensification of the Eg Raman mode. However, while the absorption edge of TiO2 was observed in the sample annealed at 500 °C, the crystalline phase was not detected by Raman spectroscopy in the same sample. Optical absorption spectroscopy provides average structural information, whereas Raman scattering spectroscopy, as a local probe, is sensitive to crystallinity and microstructures of materials. The absence of observable Raman peaks implies that annealing at lower temperatures did not produce sufficient TiO2 nanocrystals, which is verified by the SEM image in Figure 2(a). Additionally, the nanocrystals exhibit poor crystallinity, though the absorption edges of TiO2 were confirmed by optical absorption measurement.

Careful analysis of the Eg mode centered at 140 cm^−1 of the anatase-phase TiO2 as a function of annealing temperature reveals that the intensity, frequency, and linewidth (FWHM) of the Eg Raman mode are strongly dependent on the annealing treatment. The linewidth of Raman peaks indicates that the TiO2 nanofilms possess high crystallinity. The intensity of the Eg Raman mode increases with annealing temperature, accompanied by a downshift in frequency and a decrease in linewidth. The sample annealed at 900 °C exhibits a large downshift in frequency and an obvious decrease in linewidth. Similar behavior of frequency shift and linewidth decrease of the Eg Raman mode has been observed in TiO2 nanoparticles fabricated by other methods [24–28].

Proposed mechanisms to interpret this behavior include the phonon confinement effect [24, 29], internal stress/surface tension effects [28, 30], and nonstoichiometry due to oxygen deficiency [25, 26]. The pressure effect mechanism typically leads to large frequency shifts, and Raman measurements as a function of external pressure show that Raman modes undergo a downshift in frequency with increasing pressure [31]. For instance, the pressure effect induced by surrounding particles or interface stress has been successfully used to elucidate frequency shifts of Raman peaks observed in TiO2 and PbTiO3 nanoparticles [32]. The size-induced pressure effect may act similarly to external pressure on TiO2 nanoparticles. Smaller nanoparticles exhibit larger pressure contributions,

resulting in frequency downshift of the Eg anatase mode [28]. In our experiment, the size of TiO2 nanoparticles increases with annealing temperature, and pressure is gradually released during heat treatment, which should lead to frequency upshift (toward higher frequency) of the Eg mode according to the size-induced pressure effect. However, a frequency downshift with increasing annealing treatment was observed instead, implying that the pressure effect can be ruled out. According to phonon confinement effects, increased crystallite size can cause downshift in frequency and decrease in linewidth of the Eg Raman mode, suggesting that phonon confinement effects should be considered to explain the change in the Eg Raman mode.

Additionally, nonstoichiometry observed in nanophase TiO2 samples prepared by other methods [24–26] plays an important role in frequency shifts of Raman peaks, where frequency downshifts occur with decreasing oxygen deficiency. Although the TiO2 samples in this work were prepared by Ti-ion implantation and subsequent annealing in an oxygen atmosphere, oxygen deficiency, as the most common form of nonstoichiometry in TiO2, cannot be ruled out. Moreover, the downshift in frequency of the Eg anatase mode with increasing annealing temperature (decrease of oxygen deficiency) is consistent with results reported by other authors [24–26]. Oxygen deficiency decreases with increasing annealing temperature, and therefore nonstoichiometry should be taken into account when explaining changes in the Eg Raman mode in our TiO2 films.

To further confirm the formation of TiO2 nanofilms and measure the atomic ratio of Ti and O, XPS spectra of the implanted samples annealed at 800 °C were measured (Figure 4 [Figure 4: see original paper]). The peaks centered at binding energies of 458.7 eV and 464.5 eV correspond to the 2p3/2 and 1/2 core levels of Ti^4+, while the peaks centered at 530.0 eV and 532.6 eV correspond to the binding energies of Ti-O and Si-O, respectively, agreeing well with values reported by other authors [3]. The atomic ratio of Ti and O was calculated as 1:1.82, confirming the nonstoichiometry of TiO2. The color of the annealed samples changes from light blue to almost white at 900 °C, indicating a decrease in oxygen vacancies [30] and a change in film thickness according to interference phenomena in thin films.

Mechanism for the Formation of TiO2 Nanofilms: TEM Characterization

To elucidate the growth process and formation mechanism of the TiO2 nanofilms, TEM studies of the microstructure of the samples were conducted. Figure 5 [Figure 5: see original paper] shows cross-sectional TEM images of the as-implanted sample and the sample annealed at 800 °C for 2 h. A dark layer with tiny Ti nanocrystals below the surface was observed in the as-implanted sample (Figure 5(a)). After annealing at 800 °C for 2 h, a nanofilm with a thickness of 10 nm formed on the sample surface (Figure 5(b)). The selected area electron diffraction (SAED) pattern confirms the formation of an anatase-phase TiO2 nanofilm. Meanwhile, Ti atoms in the silica substrate aggregate into larger nanocrystals

according to the SAED pattern. This indicates that during annealing in O2 atmosphere, the implanted Ti atoms diffused out to the silica surface and were oxidized into TiO2 nanoparticles, while the embedded Ti nanocrystals grew larger due to the Ostwald ripening effect.

The solid-phase growth process of TiO2 nanofilms by ion implantation and subsequent thermal oxidation is similar to results reported for Zn-implanted silica and sapphire forming high-quality ZnO nanofilms on the substrate surface [14–16]. The formation of metal oxide semiconductors by metal ion implantation and subsequent thermal oxidation results from out-diffusion of the implanted metal ions to the substrate surface, where they are oxidized into metal oxide nanoparticles.

Growth of the TiO2 Nanofilms: Influence of Annealing Time

The annealing time was increased to 4 h and 6 h to further study the growth process and formation mechanism of the TiO2 nanofilms. Cross-sectional TEM images of Ti-implanted samples annealed at 800 °C for 4 h and 6 h are shown in Figure 6 [Figure 6: see original paper]. In Figure 6(b), almost all Ti atoms diffused out of the substrate to form a thicker TiO2 nanofilm with a thickness of 50 nm, and the TiO2 nanocrystals increased significantly in size. It should be noted that the TiO2 nanofilms exhibit a slow growth rate of approximately 0.15 nm/min, ensuring high crystal quality and high density of the formed nanofilms. Figure 7 [Figure 7: see original paper] shows SEM images of samples annealed at 800 °C for 4 h and 6 h. The film annealed for 6 h has a flatter surface and larger nanocrystal size than the film annealed for 4 h.

Combining TEM and SEM results, annealing time affects the surface morphology, structure, and thickness of the formed TiO2 nanofilms when samples are annealed at 800 °C. The thickness of TiO2 nanofilms increases with annealing time until all Ti atoms diffuse out of the substrate to form a thicker TiO2 nanofilm. As discussed above, the absorption edge and phase transformation of TiO2 are annealing temperature dependent, while the thickness of the TiO2 nanofilms is annealing time dependent.

Conclusion

In summary, TiO2 nanofilms were fabricated on fused silica substrates through a solid-phase growth process of Ti-ion implantation and subsequent thermal annealing in an O2 atmosphere. The growth mechanism and phase transformations of TiO2 nanofilms were discussed. The grain sizes and crystallographic phase of TiO2 nanofilms can be tailored. Higher annealing temperatures produced larger nanograin sizes, and the anatase-to-rutile phase transformation occurred at annealing temperatures above 1000 °C. The thickness of the TiO2 nanofilms is annealing time dependent and is determined by all Ti atoms diffusing out of the substrate to form thicker TiO2 nanofilms through subsequent thermal annealing under O2 atmosphere. Thus, the formation, phase, and growth of the

TiO2 nanofilms can be well tailored by controlling the annealing parameters (temperature and time). The results indicate that TiO2 nanofilms fabricated by this approach have great potential for various optical, sensing, and catalytic applications.

References

[1] Fujishima A and Honda K. Electrochemical Photolysis of Water at a Semiconductor Electrode. Nature, 1972, 238: 37-38. DOI:10.1038/238037a0

[2] Fröschl T, Hörmann U, Kubiak P, et al. High surface area crystalline titanium dioxide: potential and limits in electrochemical energy storage and catalysis. Chem Soc Rev, 2012, 41: 5313–5360. DOI: 10.1039/c2cs35013k

[3] Chen X B and Mao S S. Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications. Chem Rev, 2007, 107: 2891–2959. DOI: 10.1021/cr0500535

[4] Liang F X, Kelly T L, Luo L B, et al. Self-cleaning organic vapor sensor based on a nanoporous TiO2 interferometer. ACS Appl Mater Interfaces, 2012, 4: 4177–4183. DOI: 10.1021/am300896p

[5] Song Y Y, Gao Z D, Wang J H, et al. Multistage coloring electrochromic device based on TiO2 nanotube arrays modified with WO3 nanoparticles. Adv Funct Mater, 2011, 21: 1941–1946. DOI: 10.1002/adfm.201002258

[6] Choi H, Stathatos E and Dionysiou D D. Sol-gel preparation of mesoporous photocatalytic TiO2 films and TiO2/Al2O3 composite membranes for environmental applications. Appl Catal B-Environ, 2006, 63: 60-67. DOI: 10.1016/j.jpcatb.2005.09.012

[7] Stambolova I, Shipochka M, Blaskov V, et al. Sprayed nanostructured TiO2 films for efficient photocatalytic degradation of textile azo dye. J Photoch Photobio B, 2012, 117: 19–26. DOI:10.1016/j.jphotobiol.2012.08.006

[8] Stambolova I, Blaskov V, Shipochka M, et al. Effect of post-synthesis acid activation of TiO2 nanofilms on the photocatalytic efficiency under visible light. J Phys Conf Ser, 2014, 558: 012055. DOI:10.1088/1742-6596/558/1/012055

[9] Casu M B, Braun W, Bauchspiess K R, et al. A multi-technique investigation of TiO2 films prepared by magnetron sputtering. Surf Sci, 2008, 602: 1599–1606. DOI: 10.1016/j.susc.2008.02.030

[10] Sun H F, Wang C Y, Pang S H, et al. Photocatalytic TiO2 films prepared by chemical vapor deposition at atmospheric pressure. J Non-Cryst Solids, 2008, 354: 1440–1443. DOI: 10.1016/j.jnoncrysol.2007.01.108

[11] Yu J G and Zhao X J. Effect of substrates on the photocatalytic activity of nanometer TiO2 thin films. Mater Res Bull, 2000, 35: 1293–1301. DOI: 10.1016/S0025-5408(00)00327-5

[12] Kleiman A, Márquez A, Vera M L, et al. Photocatalytic activity of TiO2 thin films deposited by cathodic arc. Appl Catal B-Environ, 2011, 101: 676–681. DOI:10.1016/j.jpcatb.2010.11.009

[13] Amekura H, Umeda N, Sakuma Y, et al. Fabrication of ZnO nanoparticles in SiO2 by ion implantation combined with thermal oxidation. Appl Phys Lett, 2005, 87: 013109. DOI: 10.1063/1.1989442

[14] Ren F, Jiang C Z and Xiao X H. Fabrication of single-crystal ZnO film by Zn ion implantation and subsequent annealing. Nanotechnology, 2007, 18: 285609. DOI:10.1088/0957-4484/18/28/285609

[15] Xiao X H, Ren F, Fan L X, et al. ZnO single-crystal films fabricated by the oxidation of zinc-implanted sapphire. Nanotechnology, 2008, 19: 325604. DOI:10.1088/0957-4484/19/32/325604

[16] Liu Y X, Liu Y C, Shao C L, et al. Excitonic properties of ZnO nanocrystalline films prepared by oxidation of zinc-implanted silica. J Phys D Appl Phys, 2004, 37: 3025–3029. DOI:10.1088/0022-3727/37/21/013

[17] Xiang X, Chen M, Ju Y F, et al. N–TiO2 nanoparticles embedded in silica prepared by Ti ion implantation and annealing in nitrogen. Nucl Instrum Meth B, 2010, 268: 1440–1445. DOI: 10.1016/j.nimb.2010.01.023

[18] Ren F, Zhou X D, Liu Y C, et al. Fabrication and properties of TiO2 nanofilms on different substrates by a novel and universal method of Ti-ion implantation and subsequent annealing. Nanotechnology, 2013, 24: 255603. DOI:10.1088/0957-4484/24/25/255603

[19] Asahi R, Morikawa T, Ohwaki T, et al. Visible-light photocatalysis in nitrogen-doped titanium oxides. Science, 2001, 293: 269–271. DOI: 10.1126/science.1061051

[20] Zhang J, Li M J, Feng Z C, et al. UV Raman spectroscopic study on TiO2. I. phase transformation at the surface and in the bulk. J Phys Chem B, 2006, 110: 927–935. DOI: 10.1021/jp0552473

[21] Bickley R I, Gonzalez-Carreno T, Lees J S, et al. A structural investigation of titanium dioxide photocatalysts. J Solid State Chem, 1991, 92: 178–190. DOI: 10.1016/0022-4596(91)90255-G

[22] Ohsaka T, Izumi F and Fujiki Y. Raman spectrum of anatase TiO2. J Raman Spectrosc, 1978, 7: 321–324. DOI: 10.1002/jrs.1250070606

[23] Chaves A, Katiyan K S and Porto S P S. Coupled modes with A1 symmetry in tetragonal BaTiO3. Phys Rev B, 1974, 10: 3522–3533. DOI: 10.1103/PhysRevB.10.3522

[24] Zhang W F, He Y L, Zhang M S, et al. Raman scattering study on anatase TiO2 nanocrystals. J Phys D Appl Phys, 2000, 33: 912–916. DOI:10.1088/0022-3727/33/8/305

[25] Parker J C and Siegel R W. Raman microprobe study of oxidation-induced spectral changes in nanophase TiO2. J Mater Res, 1990, 5: 1246-1252. DOI:10.1557/JMR.1990.1246

[26] Parker J C and Siegel R W. Calibration of the Raman spectrum to the oxygen stoichiometry of nanophase TiO2. Appl Phys Lett, 1990, 57: 943-945. DOI: 10.1063/1.104274

[27] Bersani D, Lottici P P and Ding X Z. Phonon confinement effects in the Raman scattering by TiO2 nanocrystals. Appl Phys Lett, 1998, 72: 73-75. DOI: 10.1063/1.120648

[28] Ma W H, Lu Z and Zhang M. Investigation of structural transformations in nanophase titanium dioxide by Raman spectroscopy. Appl Phys A, 1998, 66: 621-627. DOI: 10.1007/s003390050723

[29] Barborini E, Kholmanov I N, Piseri P, et al. Engineering the nanocrystalline structure of TiO2 films by aerodynamically filtered cluster deposition. Appl Phys Lett, 2002, 81: 3052-3054. DOI: 10.1063/1.1510579

[30] Swamy V, Kuznetsov A, Dubrovinsky L S, et al. Finite-size and pressure effects on the Raman spectrum of nanocrystalline anatase TiO2. Phys Rev B, 2005, 71: 184302. DOI: 10.1103/PhysRevB.71.184302

[31] Ohsaka T, Yamaoka S and Shimomura O. Effect of hydrostatic pressure on the Raman spectrum of anatase (TiO2). Solid State Commun, 1979, 30: 345-347. DOI:10.1016/0038-1098(79)90648-3

[32] Meng J F, Zou G T, Cui Q L, et al. Raman scattering from PbTiO3 of various grain sizes at high hydrostatic pressures. J Phys Condens Matter, 1994, 6: 6543-6548. DOI:10.1088/0953-8984/6/32/015

Note: Figure translations are in progress. See original paper for figures.