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Thermal behavior of nitrided TiO_2/In_2O_3 by TG–DSC–MS combined with PulseTA

Hui-Mei Yu[a], Qing-Hong Zhang[b], Ling-Jun Qi[a],
Chang-Wei Lu[a,*], Tong-Geng Xi[a], Lan Luo[a]

[a] *Analysis & Testing Center for Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Rd., 200050 Shanghai, PR China*
[b] *State Key Laboratory of High Performance Ceramics and Superfine Structure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Rd., 200050 Shanghai, PR China*

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Abstract

TiO_2/InN (In/(Ti + In) = 6.5:100 mol) was prepared by nitridation of TiO_2/In_2O_3 by NH_3 at 580 °C for 8 h. Only the anatase TiO_2 phase was detected in the XRD measurements. The highly dispersed InN clusters on the surface of anatase TiO_2 nanocrystals were beyond the detection limit of XRD. In order to confirm the existence of InN in the products of nitridation, thermogravimetry–differential scanning calorimetry–mass spectrometry (TG–DSC–MS) coupling techniques were used for a simultaneous characterizing study of the changes of mass, enthalpy and determination of the evolved gases during the thermal decomposition of the InN and the nitrided TiO_2/In_2O_3 samples. Moreover, pulse thermal analysis (PulseTA) was combined with TG–DSC–MS for the quantitative calibration of the evolved nitrogen formed during the thermal decomposition of the InN and the nitrided TiO_2/In_2O_3. The applied technique enabled identification and quantification of the InN in the products of the nitridation of TiO_2/In_2O_3.

Keywords: Indium nitride; Nitrided TiO_2/In_2O_3; XRD; Thermal decomposition; TG–DSC–MS; PulseTA

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1. Introduction

Titania (TiO_2) photocatalysts have attracted much attention because of its good stability, non-toxic properties and extensive applications [1]. However, one of the problems preventing its large-scaled application was the requirement of the excitation of TiO_2 based samples by the ultraviolet light (wavelength less than 385 nm). Since the ultraviolet light is present in the sunlight in the amounts not exceeding 4%, the additional, energy-consumed UV lamps are needed during photocatalytic processing. Dopants such as transition metals, nitrogen, sulfur or carbon have been used to improve the photocatalytic efficiency of TiO_2 under visible light irradiation. Organic dyes or II–VI semiconductors with narrow band gap have been demonstrated to sensitize TiO_2, which can later work as visible light driven photocatalysts [2–6].

Indium nitride (InN) is one of III–V compound semiconductors in a wurtzite crystal structure and with a narrow band gap. The band gap value was still under debate [7,8], which varied from 0.7 to 1.9 eV at room temperature, depending on the defects, the carrier concentration and the oxygen incorporation in InN materials as recently reviewed by Bhuiyan et al. [9]. According to the sensitizing principle by II–VI semiconductors, it would be benefit to develop an alternative visible light driven photocatalysts titania sensitized by indium nitride. Unfortunately, InN is extremely difficult to synthesize because of the thermodynamic properties of the In + N_2 system. The high bonding energy of the N_2 molecule and the relatively low bonding energy of InN make direct growth from the constituents (In and N_2) extremely difficult [10]. Gao et al. [11] reported a novel method for the synthesis of InN powder by the direct nitridation of In_2O_3 nanoparticles. They characterized the quality of InN powder by the XRD and TEM techniques. In presented work, the TiO_2/InN sample was obtained by nitridation of TiO_2/In_2O_3 with gaseous ammonia at 580 °C for 8 h. The highly dispersed InN clusters could not

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[*] Corresponding author.
E-mail address: cwlusic@sunm.shcnc.ac.cn (C.-W. Lu).

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be detected by XRD, so it is crucial to find the method that enables the confirmation of the existence of InN in the products of nitridation.

In this paper, TG–DSC–MS [12–15] combined with PulseTA techniques were used to confirm the existence and quantification of InN in the products of the nitridation of TiO_2/In_2O_3.

2. Experimental

2.1. Preparation of InN powder and the TiO_2/InN powder

Indium nitrate (99.5% $In(NO_3)_3·4.5H_2O$) solution with concentration of 0.3 mol/L was used as the main raw material. Firstly, the aqueous solution was neutralized to pH 8 with the ammonia solution of 1.0 mol/L at room temperature. The precipitate was separated from the solution by filtration, and repeatedly washed with distilled water. Then, the white filtration cake was dried at 110 °C for 24 h, and calcined at 450 °C for 2 h to obtain crystalline In_2O_3 nanoparticles. For the preparation of TiO_2/In_2O_3 sample, titanium tetrachloride (98% $TiCl_4$) and indium nitrate (99.5% $In(NO_3)_3·4.5H_2O$) were used as the raw materials using the similar procedure as those applied for the synthesis of In_2O_3 nanoparticles. The InN powder with the particle size of 40–300 nm was obtained by the nitridation of In_2O_3 with ammonia at 600 °C for 8 h according to the procedure described in Ref. [11]. By using the same process as for the synthesis of the InN, the TiO_2/InN samples with particle size of 20–30 nm were obtained by the nitridation of TiO_2/In_2O_3 with ammonia at 580–600 °C for 8 h. The results of TG–DSC–MS indicated that complete nitridation of In_2O_3 in TiO_2/In_2O_3 was performed at 580 °C for 8 h, suggesting the complete nitridation temperature of 580 °C for In_2O_3 in TiO_2/In_2O_3 was lower than that of 600 °C for bare In_2O_3. In this paper, the results for the sample TiO_2/In_2O_3 after nitridation at 580 °C were given and compared to that of InN obtianed via nitridation of In_2O_3 at 600 °C for 8 h.

2.2. TG–DSC–MS measurements

Netzsch STA 449C TG–DSC thermoanalyzer coupled with Balzers Thermostar Quadrupole Mass Spectrometer was used in the experiments. The quartz capillary was used as the interface between thermoanalyzer and the quadrupole MS. The mass of the InN and the nitrided TiO_2/In_2O_3 samples was 16.69 and 15.25 mg, respectively. The argon with a flow rate of 20 mL/min was used as the carrier gas. The temperature range was from room temperature to 1000 °C. The vacuum in the quadrupole MS was 10^{-4} Pa. The multiple ion detector (MID) mode was used in the MS measurements.

2.3. PulseTA measurements

The PulseTA technique has been developed in 1997 [15] and put on the market by Netzsch Company in Germany. PulseTA enables the quantification of the mass spectrometric signals of the evolved gases in the TA–MS systems [16,17]. Introducing into the TA–MS system a known amount of the calibration gas and determining the relationship between the amount of the injected gas and the observed integral signal, it is possible later to quantify the MS signals resulting from evolution of the unknown amount of evolved gases during the decomposition.

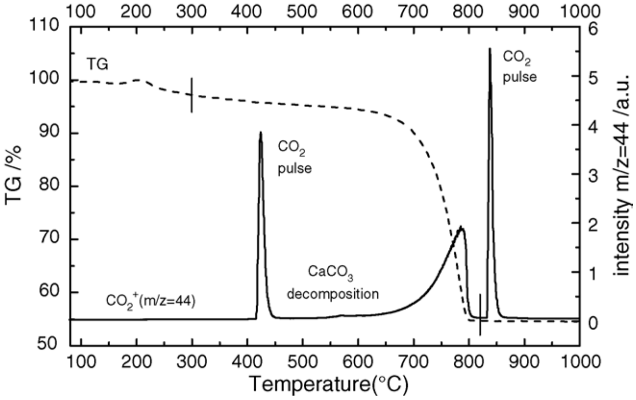

Fig. 1. The TG–MS curves of the $CaCO_3$ at the heating rate of 10 K/min.

Maciejewski and Baiker confirmed the accuracy of the quantitative calibration of the mass spectrometric signals for the PulseTA in combined TA–MS system [17]. We verified the accuracy of this method by coupling the TA–MS and PulseTA in our laboratory. The TG–MS curves of the $CaCO_3$ calcined at the heating rate of 10 K/min is shown in Fig. 1. $CaCO_3$ (5.59 mg) decomposed under argon with a flow rate of 20 mL/min. The TG curve shows 2.38 mg mass losses (about 42.50%) occurring in one step. The mean value of the integral intensities of the injected pulses (0.5 mL) was 5.349E−07 A s. The integral intensity of the MS signal of evolved CO_2 was 1.360E−06 A s. The temperature of the injected gas was 14 °C. The measured amount of CO_2 formed during $CaCO_3$ decomposition was 2.39 mg, which is consistent with the amount measured by TG (2.38 mg). The difference between these values and the stoichiometric amount of the CO_2 in the sample (2.46 mg) is due to the presence of the traces of the water in the $CaCO_3$ sample. The mass loss in the range room temperature to 300 °C on TG curve shown in Fig. 1 was 0.15 mg (2.61%). The results confirmed the accuracy of the quantification method of the MS signals in the system TA–MS combined with the PulseTA.

The same experimental setup was used for the determination of the presence and quantification of the amount of InN in the nitrided TiO_2/In_2O_3 samples. For the calibration the nitrogen (99.999%) was used. The injection volume of N_2 was 0.5 mL and the N_2 calibration pulses were injected two or three times during the experiments.

3. Results and discussion

3.1. XRD results

Fig. 2 shows the XRD patterns of TiO_2/In_2O_3 (In/(In + Ti) = 6.5/100 mol) after calcination at 450 °C for 2 h in air and TiO_2/InN (In/(In + Ti) = 6.5/100 mol) after nitridation of TiO_2/In_2O_3 at 580 °C for 8 h in the flowing NH_3. For comparison, the XRD patterns of InN obtained by nitridation of

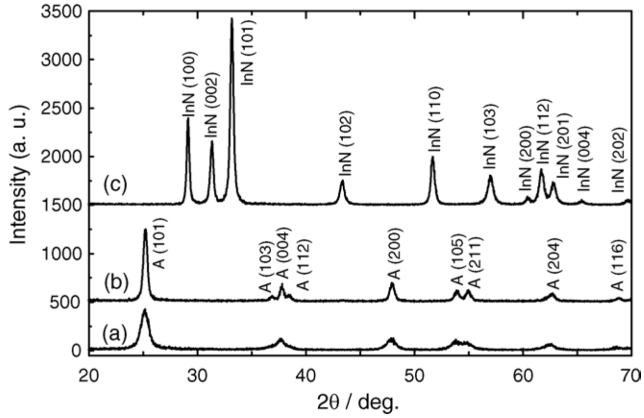

Fig. 2. The XRD patterns of (a) TiO_2/In_2O_3 (In/(In + Ti) = 6.5/100) after calcination at 450 °C for 2 h in air, (b) TiO_2/InN (In/(In + Ti) = 6.5/100) after nitridation of TiO_2/In_2O_3 at 580 °C for 8 h in the flowing NH_3, (c) InN obtained by nitridation of In_2O_3 nanoparticles at 600 °C for 8 h in the flowing NH_3. 'A' denotes anatase TiO_2.

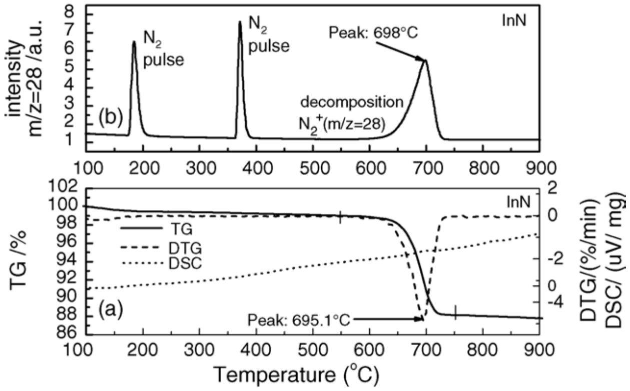

Fig. 3. The TG–DTG–DSC curves (a) and the MS curve (b) of the InN powder at the heating rate of 20 K/min. The 0.5-mL pulses of N_2 were used for the calibration of the MS signal.

In_2O_3 nanoparticles at 600 °C for 8 h in the flowing NH_3 was also given in this figure. In Fig. 2(a), one can see the broadening of XRD peaks of the anatase phase TiO_2 caused by the very small particles of nanosized TiO_2. As shown in Fig. 2(b) XRD result indicates the presence of only anatase phase TiO_2 in the nitrided powder. The lack of the InN patterns may be due to the high dispersion of InN in the TiO_2 matrix and too low amount of InN in the products of nitridation to be detected by XRD. In order to verify the presence of InN in the products of nitridation, we made the further study of the thermal behavior of the InN and nitrided TiO_2/In_2O_3 by TG–DSC–MS combined with PulseTA technique.

3.2. TG–DTG–DSC–MS and PulseTA investigation of the InN powder

Before studying the existence of the InN in the products of the TiO_2/In_2O_3 nitridation, we investigated the thermal behavior of the InN powder. The results are depicted in Fig. 3. The TG results show (Fig. 3a) that the mass loss was 1.82 mg at 550–750 °C (about 10.90%). The stoichiometric amount of nitrogen was 1.81 mg. The measured result by TG was closed to the stoichiometric value. The derivative thermogravimetry (DTG) curve shows the maximum of the peak at 695.1 °C. Due to the low bonding energy of InN (about 4.6 kcal/mol [18]), the DSC curve does not show any endothermic event resulting from the thermal effect of the decomposition. The MS signal recorded during the InN decomposition (Fig. 3b) shows the N_2^+ ($m/z = 28$) ion mass spectrometric peak in the range of 550–750 °C (peak at 698 °C). The integral intensity of the $m/z = 28$ ion current resulting from the decomposition of InN and evolution of nitrogen was 5.574E−07 A s. The mean value of the integral intensities of the injected pulses of nitrogen (0.5 mL, temperature of injection 20 °C) was 1.900E−07 A s. The amount of N_2 formed during the InN decomposition calculated from these data corresponds to 1.71 mg. The mass of the InN sample was 16.69 mg. The stoichiometric amount of nitrogen is 1.81 mg. The TG–DTG–DSC–MS results indicate that the thermal decomposition of the InN proceeds in one step between ca. 550 and 750 °C. The DTG peak has the maximum at 695.1 °C. Therefore, the thermal decomposition process of the InN can be expressed as:

$$2\mathrm{InN} = 2\mathrm{In} + \mathrm{N_2}\uparrow$$

The PulseTA results of the studies of InN decomposition under different heating rates are submitted in Table 1. The results presented in this table indicate that the amount of evolved nitrogen in the experiments carried out with different heating rates is equal to ca. 95% of the amount of the nitrogen which should be present in the InN sample. Unlike the clean InN sample, the influence of oxygen should be taken into account. It is found that InN can strongly oxidize when it is exposed to air [19] or even residual gases in high vacuum environment [20]. We also measured mass to charge ($m/z = 16$) positive ions by TA–MS combined with PulseTA techniques. In each channels, the different m/z numbers were proposed. The results showed that the

Table 1
The PulseTA results for the InN powder under different heating rates

Heating rate (K/min)	Sample mass (mg)	N_2 pulse (1, $\times10^{-7}$ A s)	N_2 pulse (2, $\times10^{-7}$ A s)	N_2 pulse (3, $\times10^{-7}$ A s)	N_2 pulse (average, $\times10^{-7}$ A s)	Decomposed N_2 ($\times10^{-7}$ A s)	Stoichiometric amount of nitrogen (mg)	Measured mass of nitrogen (mg)
5	20.30	1.985	1.964	1.956	1.968	7.377	2.21	2.18
10	15.43	2.053	1.985	1.936	1.991	5.403	1.68	1.58
15	11.55	2.005	1.963	1.969	1.979	4.081	1.26	1.20
20	16.69	1.919	1.881	–	1.990	5.574	1.81	1.71

Pulse volume, 0.5 mL and injection temperature, 20 °C.

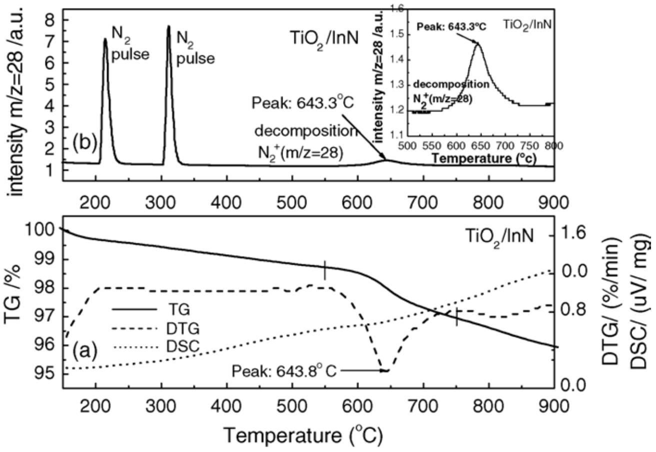

Fig. 4. The TG–DTG–DSC curves: (a) and the MS curve (b) of the nitrided TiO_2/In_2O_3 at the heating rate of 20 K/min. The 0.5-mL pulses of N_2 were used for the calibration of the MS signal.

integral intensity of the nitrogen ($m/z = 28$) ion current resulting from the decomposition of InN was 5.57E−06 A s. The integral intensity of the oxygen ($m/z = 16$) ion current was about 1.5E−08 A s at 250–420 °C and 1.09E−08 A s at 500–750 °C, which may be resulted from an oxidized surface shell. The integral intensity of the nitrogen was at least 100 times stronger than that of oxygen. Therefore, the amount of oxygen was small. The influence of oxygen is needed to study further.

3.3. *TG–DTG–DSC–MS and PulseTA investigation of the products of TiO_2/In_2O_3 nitridation*

Fig. 4(a) shows the TG–DTG–DSC curves of the product of TiO_2/In_2O_3 nitridation. The TG signals indicate that the mass loss changes between 550 and 750 °C was 0.27 mg (about 1.8%), its stoichiometric mass of N_2 in the TiO_2/InN sample amounts to 0.17 mg. We can see the difference between the mass loss value measured by TG and its stoichiometric mass loss value. When the temperature was over 750 °C, the TG curve for TiO_2/InN still appeared the mass losses. It may be related to the particle size effect of the nano-powder at higher temperature. The temperature of the DTG peak was 643.8 °C, which was lower than for the InN (695.1 °C). There was no endothermic peak in the DSC curve. In Fig. 4(b), the MS curve recorded during the nitrided TiO_2/In_2O_3 decomposition shows the $N_2{}^+$ ($m/z = 28$) ion mass spectrometric peak in the range of 550–750 °C (peak at 643.3 °C). The integral intensity of the signal of $N_2{}^+$ ion current was 4.457E−08 A s. The temperature of the injected nitrogen used for the calibration of the MS signal was 20 °C. The mean integral intensity of the injected 0.5 mL pulses of N_2 was 2.025E−07 A s. The detected amount of N_2 formed during the decomposition of the nitrided TiO_2/In_2O_3 sample was 0.13 mg. The stoichiometric mass of N_2 in the TiO_2/InN sample assuming total nitridation of In_2O_3 amounts to 0.17 mg.

3.4. *Discussion*

The thermal behaviors of oxidized InN and clean InN samples have been studied, respectively, by Ambacher et al. [21] and Dimakis et al. [22]. Ambacher et al. measured the decomposition of InN prepared by metal organic chemical vapor deposition by heating the sample and recording the partial pressure of relevant gases. The products of desorption and thermal decomposition were measured using a Hiden HAL2/511 type quadropole mass spectrometer. In their results, the maximum nitrogen desorption rate was reached at 685 °C (T_{max}) for the 0.5 μm thick InN layers. Our samples have been exposed to the air and the results ($T_{max} = 698$ °C) measured by quadropole mass spectrometer were close to that of Ref. [21]. Therefore, with the help of TA–MS coupling techniques, we verified the existence of InN by the nitridation of In_2O_3.

The InN and the TiO_2/InN samples were obtained by the nitridation of In_2O_3 or TiO_2/In_2O_3 by ammonia at temperatures of 600 and 580 °C, respectively. The reaction can be expressed as:

$$In_2O_3 + 2NH_3 = 2InN + 3H_2O$$

As confirmed by XRD, obtained InN has the wurtzite-type crystal structure as shown in Fig. 2(c). However, no XRD peaks were detected in the product of TiO_2/In_2O_3 nitridation as shown in Fig. 2(b). The color of the nitrided powder with changed from white into brown, suggesting that the nitridation occurred at the temperature of the reaction. We confirmed the formation of the InN by the TG–DSC–MS combined with the PulseTA experiments. In both samples i.e. the InN powder and the product of TiO_2/In_2O_3 nitridation the decomposition of indium nitride, resulting in the nitrogen evolution, occurs in the same temperature range 550–750 °C. This finding confirms that the evolution of nitrogen from nitrided TiO_2/In_2O_3 was caused by the thermal decomposition of the InN but not by the desorption of possibly adsorbed nitrogen on titania. The amount of the evolved N_2 was close to the stoichiometric value during the decomposition of the InN sample, but slightly lower (ca. 75% of the stoichiometric value) in the case of the nitrided TiO_2/In_2O_3 sample. One must note that the maximal rate of the nitrogen evolution (peak on the DTG curve) was distinctly lower in nitrided TiO_2/In_2O_3 comparing to the InN being 643.3 and 695.1 °C, respectively. This observation could be explained by the difference of the particle size of both powders. In general, both initial and final thermal decomposition temperature decreased with decreasing particle size of the sample [23]. In our experiments, the particle size of the InN was in the range of 40–300 nm, whereas the particle size of the nitrided TiO_2/In_2O_3 was 20–30 nm. Therefore, the peak position in the nitrided TiO_2/In_2O_3 sample shifted to the lower temperature than that in the InN powder.

Due to the continuous mass change at higher temperature for the nitrided TiO_2/In_2O_3 sample, the application of the TG signal for the characterization of the InN decomposition would be impossible. Only the quantification of the MS signal done by PulseTA technique allowed the determination of evolved nitrogen confirmed formation of indium nitride during TiO_2/In_2O_3 nitridation.

4. Conclusions

The TiO_2/InN powder was prepared by nitridation of TiO_2/In_2O_3 with gaseous NH_3. The amount of highly dispersed

InN in the nitrided sample was beyond the detectable level of XRD, and its existence and amount of the N_2 in the product could be confirmed by the TG–DSC–MS and PulseTA technique only. The presented results indicate that combining of TG–DSC–MS with PulseTA technique offers a very good tool for the confirmation and quantification of the indium nitride. Moreover, this method is going to be applied in our laboratory for the investigation of the thermal behavior of InN-containing III–V semiconductors.

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