

## Synthesis and Characterization of Amorphous Phosphorus Nitride

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Amorphous phosphorus nitride ( $P_3N_5$ ) has been synthesized from the reaction of  $PCl_5$  and  $NaN_3$  in an autoclave at 190–300 °C. XPS, IR and TEM revealed that the product was amorphous  $P_3N_5$  with flake-like morphology. The influences of experimental conditions were discussed.

Phosphorus nitride ( $P_3N_5$ ) has been studied for many years,<sup>1–4</sup> but only recently pure, crystalline and well-defined  $P_3N_5$  was obtained and its crystal structure was known.<sup>5–7</sup> Recently, phosphorus nitride was focused as metal-insulator–semiconductor (MIS),<sup>8–11</sup> which has high dielectric strength of  $\sim 10^7$  V  $cm^{-1}$  and remarkable chemical stability.<sup>12,13</sup>

Conventionally, phosphorus nitride is synthesized by many methods at high temperature, such as the element reaction<sup>14</sup> and the reactions between P compounds (containing halogen or free of halogen) and N-source ( $NH_3$  or  $N_2$ ).<sup>4</sup> Recently, thermal, plasma and photochemical vapor deposition (CVD) techniques for the formation of phosphorus nitride have been reported,<sup>8–11,13</sup> and precursor decomposition method was used to synthesize pure, crystalline and well-defined phosphorus nitride.<sup>5–7</sup>

Herein, we report a new method for the preparation of amorphous phosphorus nitride at 190–300 °C by using analytically grade  $PCl_5$  as P-source and  $NaN_3$  as N-source. The synthetic reaction was carried out in an autoclave associated with the reaction:



All manipulations were carried out in a dry glove box with  $N_2$  gas flowing. In a typical experiment, analytical grade  $PCl_5$  (0.005 mol) and  $NaN_3$  (0.025 mol) were put in a titanium alloy autoclave of 50 mL capacity. The autoclave was maintained at 250 °C for 15 h and then cooled to room temperature naturally. The product was collected, washed with carbon disulfide, benzene, absolute alcohol and distilled water several times and dried in vacuum at 100 °C for 4 h. Light yellow powders were obtained.

The X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer with an exciting source Mg  $K\alpha$  (1253.6 eV) in high vacuum ( $5 \times 10^{-9}$  Pa). The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C 1s to 284.70 eV. The binding energies of P 2p and N 1s are 133.4 and 398.8 eV, which are close to the values of the phosphorus nitride.<sup>13,15,16</sup> The quantification of peaks confirmed that the atomic ratio of P : N was 3:4.91. No peaks of chlorine and sodium were observed in the survey spectra.

The infrared spectra were recorded on a Magna IR-750FT spectrometer in the 400–4000  $cm^{-1}$  range (Figure 1). The

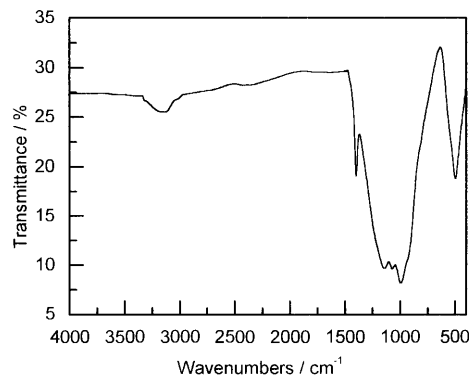


Figure 1. IR spectra of amorphous phosphorus nitride.

absorption bands at 500, 900–1150, and 1400  $cm^{-1}$ , which indicated the presence of single and double phosphorus–nitride bonds, are in agreement with the reported.<sup>5,7,13</sup> This result, together with the XPS data confirmed that the sample was phosphorus nitride. A weak absorption at 3100–3500  $cm^{-1}$  was observed, which was attributed to the O–H vibration of water because hydrogen does not exist in the reaction and so N–H band could not be formed.

The morphology of the sample was observed by transmission electron microscopy (TEM) using on Hitachi H-800 transmission electron microscope. The TEM image of the sample is shown in Figure 2, which reveals that the sample has flake-like

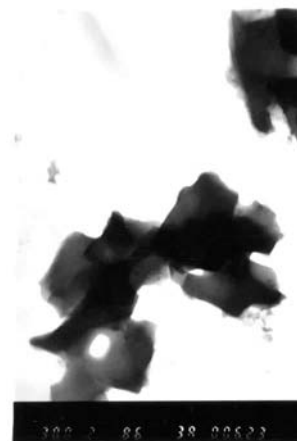


Figure 2. TEM image of amorphous phosphorus nitride.

morphology. Selected electron diffraction (SED) of the sample could not be obtained which indicated that the sample was amorphous.

The influences of temperature, time and the amounts of the reactants on the synthesis of amorphous phosphorus nitride were studied. If the temperature is lower than 190 °C, the reaction is very incomplete and little product can be obtained. But at the temperature above 300 °C, too much yellow phosphorus is yielded. The reaction is also incomplete if the time is shorter than 10 h. A longer time than 15 h has no significant effect on the formation and quality of phosphorus nitride. When  $\text{PCl}_5$  (0.015 mol) and  $\text{NaN}_3$  (0.075 mol) are used in the reaction, yellow phosphorus instead of phosphorus nitride is yielded, which may be due to increased pressure in the vessel. It is believed that high temperature and pressure make for the formation of yellow phosphorus, and appropriate temperature (190–300 °C), time (10–15 h) and pressure (lower) are necessary to the synthesis of phosphorus nitride.

Though in our experiments all of the products are amorphous and it seems to be impossible to get crystalline  $\text{P}_3\text{N}_5$  through this reaction, the crystallization of amorphous  $\text{P}_3\text{N}_5$  may be realizable by a suitable treatment. High pressure sintering with  $\text{N}_2$  flowing is a considerable method and we will do some experiments for this purpose.

In summary, amorphous phosphorus nitride was synthesized through a reaction between  $\text{PCl}_5$  and  $\text{NaN}_3$  at 190–300 °C. XPS, IR and TEM revealed that the product was amorphous  $\text{P}_3\text{N}_5$  with flake-like morphology. The influences of temperature, time and the amounts of the reactants were discussed.

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