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Catalytic Decomposition of Hydrazine on Germanium

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SUMMARY

The decomposition of hydrazine vapors on the surface of single-crystalline germanium at 650°C is studied. This catalytic reaction proceeds according to the scheme $3N_2H_4 \rightarrow 4NH_3+N_2$. Ammonia corresponds to an equimolar amount of chemisorbed hydrazine ($nN_2H_4(g) \rightarrow nNH_3(g)+(NH)_n(ads)$)..

Keywords: Hydrazine, Germanium, Catalytic decomposition.

INTRODUCTION

Hydrazine is one of the most chemically active substances - a strong reducing agent. He has wide application in various fields of industry, technology, medicine, etc. and has been intensively studied both previously and currently [1-12]. Liquid N_2H_4 is very hygroscopicand has a noticeable ability to absorb oxygen and carbon dioxide from the air. It is called "high purity" when the water content does not exceed 1 wt.% and "ultra-pure" - with a maximum of 0.5 wt.% H_2O. The concentration of water in hydrazine is estimated by the density, melting point, or refractive index of the mixture. However, literature data on these parameters are different, due to the difficulty of accurately determining the physical characteristics of pure hydrazine.(*)

Hydrazine is easily decomposed by heat and radiation, especially in the presence of catalysts [13-17]. The general form of this reaction is given by the equation:

$$3N_2H_4 \rightarrow 4(1-x)NH_3+(1+2x)N_2+6xH_2. \qquad (1)$$

Depending on external conditions (temperature, pressure, catalyst, electromagnetic radiation, electric discharge, etc.) $0 \leq x \leq 1$.(**)

The catalytic decomposition of hydrazine on the surface of germanium has been studied relatively little and there is data when carrying out the reaction up to 80°C. In early work [18], powders of Ge of n- and p-type conductivity were used. It was found that the decomposition products were ammonia and nitrogen. The type of conductivity did not affect the catalytic properties.

The paper presented here examines the decomposition of hydrazine on the surface of single-crystalline germanium at 650°C.

REAGENTS

Commertial hydrazine-hydrate containing 50 mol.% (36 wt.%) water was distilled using the Raschig's method with improvement. In particular, before distillation, it was boiled with NaOH in an inert atmosphere of nitrogen at a temperature of 120°C for two hours. Hydrazine purified in this way had a density of $\rho \cong 1.0024$ g/cm^3 and a refractive index of$n_D^{20} \cong 1.4705$. According to the literature, $n_D^{20} \cong 1.471$ corresponds to 100% N_2H_4. However, this can be considered not entirely correct (see appendix).

Plates of single-crystalline germanium doped with antimony (charge carrier concentration $n \cong 2{\cdot}10^{14}$cm^{-3}) had a resistivity of ≅35 Ohm·cm. The crystallographic orientation of Ge plates are (111) or (100). They were previously degreased in boiling toluene, etched in liquid etchant CP-4A ($HF:HNO_3:CH_3COOH$=1:15:1) for 4-5 minutes and washed in running distilled water.

RESULTS

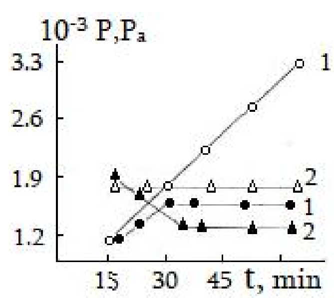
As mentioned above, hydrazine decomposes on germanium according to the scheme [18]:

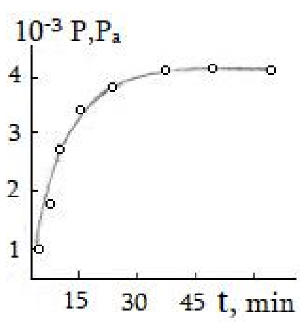
$$3N_2H_4 \rightarrow NH_3 + N_2. \qquad (2)$$

Dissociative chemisorption of N_2H_4 without nitride formation can be represented as:

$$nN_2H_4(g) \rightarrow nNH_3(g) + (NH)_n(ads). \qquad (3)$$

The resulting ammonia corresponds to an equimolar amount of chemisorbed hydrazine. As a result, the total change of pressure is determined only by the decomposition reaction.





(a) (b)

Figure 1. (a) Kinetic curves of hydrogen (1) and ammonia (2) accumulation during the decomposition of hydrazine in the presence of germanium (●) and without it (o). (b) Kinetic curve of the total change of pressure of gaseous products at 650°C.

Figure 1 shows the kinetic curves of the accumulation of hydrogen and ammonia at 650°C. It can be seen that the amount of ammonia is constant in the absence of germanium, and in its presence gradually decreases. The hydrogen content in the presence of Ge increases sharply, and in its absence it first increases and then decreases.

Thermodynamic calculation of the change of free energy showed that reaction (1) at x = 0.25 has almost the same probability as reaction (2). However, the discovered fact of hydrogen evolution gives preference to reaction (1):(***)

$$2N_2H_4 \rightarrow 2NH_3 + N_2 + H_2. \qquad (4)$$

A sharp increase of the amount of hydrogen and a decrease of the amount of ammonia in the presence of germanium can be associated with a heterogeneous reaction:(****)

$$3Ge + 4NH_3 \rightarrow Ge_3N_4 + 6H_2. \qquad (5)$$

The study of high-temperature decomposition of hydrazine was also carried out using IR absorption spectra. Figure 2 shows the IR spectra of N_2H_4 vapor, demonstrating the dynamics of its decomposition at 650°C. Curve 1 corresponds to hydrazine vapor, curves 2 and 3 to hydrazine heated for 15 and 30 minutes, and curve 4 to pure ammonia. These spectra indicate that the decomposition of hydrazine at 650°C occurs mainly during the first 15 minutes and is completely completed within 30 minutes.

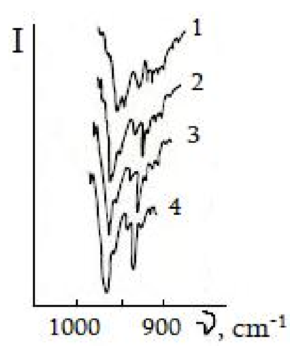


Figure 2. Dynamics of hydrazine decomposition at 650°C.

Footnote belows:

(*)According to various authors, the density of liquid hydrazine at 25°C is 1.0045, 1.0036 and 1.0024, 1.008 g/cm^3 at 23°C. The melting point of the system N_2H_4/H_2O: 1, 1.4, 1.53, 1.6-1.7, 1.8, 1.85 and 2°C.

(**)On alkaline catalysts x=1, on some semiconductor catalysts (Ga, Ga_2Se_3 and others), as well as on some metals (Te, Pt) x=0, on some other semiconductors (V_2O_5, Ga_2Te_3 and others), as well as on acid catalysts $0<x<1$, during decomposition using a spark x = 0.38, and during bombardment with α-particles x = 0.12-0.22.

(***)For reaction (2) $\Delta G \cong 220.5$ kJ/mol and for reaction (4) $\Delta G \cong 222.6$ kJ/mol.

(****)This reaction is the main method for producing of germanium nitride, which has applications in micro- and nanoelectronics, photoluminescence, energy storage, photocatalysis and others [19-24].

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ჰიდრაზინის კატალიზური დაშლა გერმანიუმზე

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რეზიუმე

შესწავლილია ჰიდრაზინის ორთქლის დაშლა მონოკრისტალური გერმანიუმის ზედაპირზე 650°C ტემპერატურისათვის. ეს კატალიზური რეაქცია მიმდინარეობს $3N_2H_4 \rightarrow 4NH_3 + N_2$ სქემის მიხედვით. ამიაკი შეესაბამება ქემოსორბირებული ჰიდრაზინის ექვიმოლარულ რაოდენობას შემდეგი სქემით: $nN2H4(g) \rightarrow nNH3(g) + (NH)n(ads)$.

საკვანძო სიტყვები: ჰიდრაზინი, გერმანიუმი, კატალიზური დაშლა