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Catalysis of Formic Acid Decomposition by Surface-Doped Germanium

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The decomposition of formic acid in the presence of a germanium catalyst was studied. Germanium samples having carrier levels which varied by at least two orders of magnitude were prepared by bulk doping. The formic acid decomposition was not affected by the variation in carrier concentration.

Germanium having doped surface layers was also prepared. Catalytic effects could be correlated with the doping. Activity was found to vary with the amount of surface doping.

INTRODUCTION

For several years there has been interest in the catalytic activity of semiconducting materials. Of especial interest has been the promise of control of catalytic activity that seemed to be offered by control of the electronic properties of these materials with doping (*1*). Recent evidence however, indicates that for some reactions or for some semiconductors, the electronic properties of a material are only loosely related to its catalytic properties (*2*, *3*).

Aigueperse and Teichner (*3*) have shown that the activating effects of surface doping and bulk doping differ. Their results raise doubt as to whether any effects are derived from bulk doping. These authors found that zinc oxide bulk-doped with Ga^{3+} (n-type) or Li^+ (p-type) and activated by heating in vacuum, had no effect on the activation energy of ethylene hydrogenation. In this experiment the electronic conductivity of the oxide was altered, but catalytic activity was the same as that of an undoped zinc oxide catalyst treated identically. The predominant factor in this catalyzed reaction appears to be the presence at the oxide surface of interstitial zinc resulting from vacuum heat treatment. These nonstoichiometric or doped surface layers affect catalytic activity so as to completely mask effects from bulk doping.

Elemental semiconductors bulk-doped to various conductivity levels have been used as catalysts in several studies. In recent work of Moore, Smith, and Taylor (*4*) bulk-doped germanium was studied as a catalyst for the decomposition of formic acid and for hydrogen–deuterium exchange. While the latter reaction showed definite changes in activation energy as bulk doping was varied, formic acid decomposition revealed no clear relationship between doping level and chemical activity.

It was the purpose of the present study to compare the effects of bulk and surface doping on the activity of a germanium catalyst. The decomposition of formic acid was used to measure activity.

The germanium samples were prepared as catalysts under differing conditions. If bulk doping was to be studied, a quartz reactor was used. Since Pyrex glass and metal ions induce p-type surface-doped layers on germanium and silicon (*5*), all Pyrex wool and Pyrex parts were removed from the reactor and care was taken to exclude metal ions from contact with the germanium.

To achieve surface-doped layers the

germanium was heated in the presence of Pyrex wool or in the presence of gallium vapors. The former method is experimentally simpler, but the latter can be controlled by adjusting the temperature of the gallium source.

EXPERIMENTAL

Materials and Preparations. The germanium used in this work was prepared at Texas Instruments by the horizontal float zone technique. The samples were gallium doped to $\rho = 0.11 \pm 0.03$ ohm-cm or $\rho = 0.002 \pm 0.001$ ohm-cm resistivity. These resistivities correspond to room-temperature carrier concentrations of 3×10^{16} and 1×10^{18} atoms/cm^3, respectively. The formic acid used was Baker reagent grade. It was dried over Drierite and distilled directly into the storage vessel of the reactor. The fraction from 99.5°C to 101°C was taken as reactant.

The germanium was crushed to an average particle diameter of ⅛ to ¹⁄₁₆ inch. This material was etched 1 min with CP-4, boiled in 12 meg-ohm water for 30 min to remove adsorbed hydrofluoric acid, immersed in a mixture of equal parts methanol and concentrated hydrochloric acid to remove adsorbed metal ions, rinsed, and dried in a vacuum desiccator. The sample was then placed in the sample holder in the reactor and thoroughly flushed with dried helium.

Equipment. The catalytic activity of the variously treated samples was measured in an apparatus similar to the differential microreactor of Schwab (*6*) and Germain *et al.* (*7*) (see Fig. 1). The boiler in this apparatus accommodates approximately 700 ml. To achieve rapid boiling, the outside of the boiler was held at about 97°C. This large boiler was necessary to avoid transient effects during initial heating and when the liquid level began to drop below the heater. The germanium sample was held in place in the furnace region by plugs of quartz wool. The region marked "trap" in Fig. 1 actually represents two traps: one to absorb water and formic acid (Linde Molecular Sieve 5A) and a second to absorb CO_2 (Ascarite).

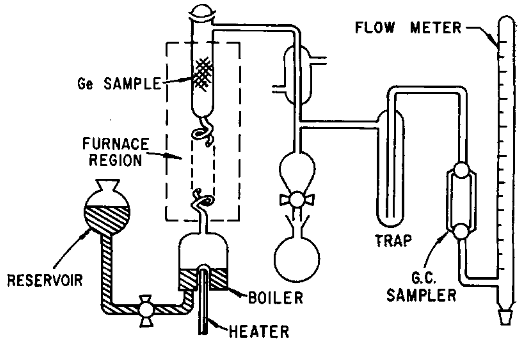

FIG. 1. Apparatus for the study of germanium samples prepared *in situ* for formic acid decomposition.

Germanium samples doped using Pyrex glass were prepared *in situ,* in which case a Pyrex reactor was used and Pyrex wool substituted for the quartz wool plugs supporting the catalyst.

A quartz reactor was used as the doping chamber for doping with vaporized gallium. The system was set up horizontally and a boat to contain the gallium was placed at what is normally the upper end. Best results were obtained by holding the gallium source at 400°C and the germanium at 800–900°C. This treatment, if continued during 4 hr yielded germanium doped to just under the solubility limit (5×10^{20} carriers/cc). Further treatment caused precipitation of a Ge–Ga alloy.

Measurements. Decomposition rates were measured in terms of product gas flow rates. The data are in units of cm^3/min. The method allows a reproducibility of about ± 2 cm^3/min (or ± 0.1 mmole/min) activity. The results are reported in mmole/g min to allow comparing samples of different weights. Specific areas of the various samples were found to be similar—about 0.10 m^2/g—after 15 hr heating at the elevated temperature. Examination of the germanium surfaces revealed extensive pitting which accounts for this rather large area. Thermal decomposition, in the absence of the catalyst, is about 0.3 mmole/min and is but slightly affected by varying flow rates or temperatures in our range of study (300–400°C). Formic acid has available two paths for decomposition: the formation of CO_2 and hydrogen and the formation of CO and H_2O. The Ascarite–molecular sieve trapping system removed water and carbon dioxide from the product gas stream. Thus, the rate of product gas flow directly reflected the rate of formic acid decomposition. Analysis of the gas stream for the H_2/CO ratio then allowed the individual rates to be found.

Surface area measurements were performed using krypton as adsorbate and a conventional BET apparatus. The krypton saturation pressures are the extrapolated liquid pressures. The surface area measurements are precise to about ±10%.

In a system such as this there is always the problem of operating at reactant gas flow rates where the decomposition is reaction-controlled rather than diffusion-controlled. To achieve reaction control, the formic acid flow rate was kept low at the beginning of several runs and then progressively increased. Data were taken when the decomposition rate no longer was affected by changing the reactant flow rate. In all experiments reactant flow rates were regulated to provide reaction-controlled decomposition.

RESULTS

Figure 2 shows the rates of decomposition of formic acid at various temperatures for samples annealed in the quartz reactor. When the reactor is of quartz the possibility of surface-doping of the sample is removed.

The rates of decomposition observed here were quite low—in some cases nearly that observed as the background decomposition due to the reactor and quartz wool alone. For comparison in this figure we have included the activity observed for a sample which was annealed 100 hr in a Pyrex reaction chamber. The sample's activity was greatly enhanced by the treatment.

In Fig. 3 the variation of reaction rate with temperature is shown for another germanium sample annealed at 600° ± 10°C in Pyrex glass. In this case annealing was periodically interrupted and the variation of reaction rate with temperature determined. After about 80 hr of annealing

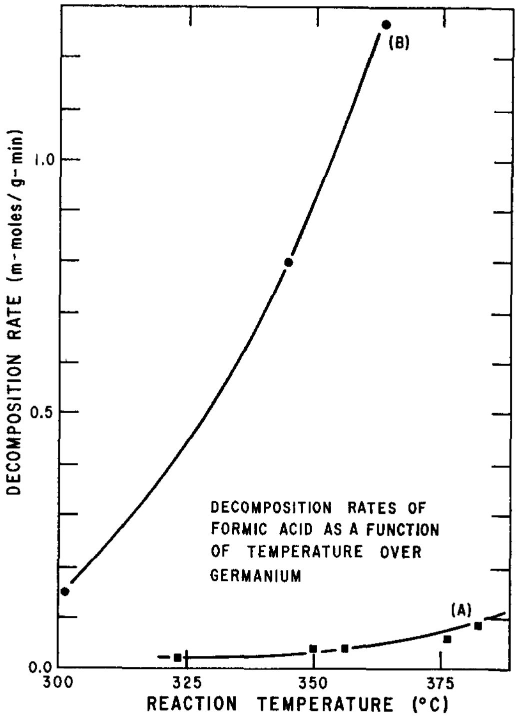

FIG. 2. Decomposition of formic acid over variously treated germanium samples. (A) Germanium annealed at 600°C during 50 hr under a helium ambient in quartz apparatus. (B) Germanium annealed at 600°C during 100 hr under a helium ambient in Pyrex apparatus.

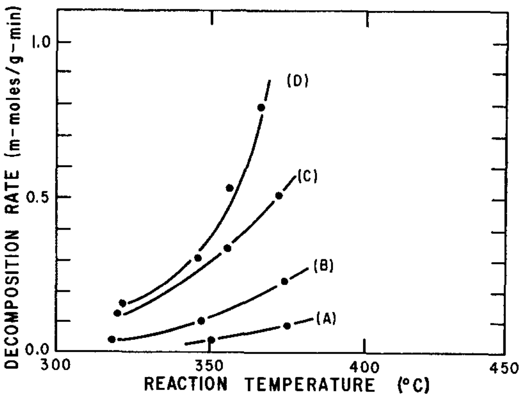

FIG. 3. Decomposition of formic acid over a germanium sample annealed at 600°C under a helium ambient in a Pyrex reactor. Annealing times (A) 16 hr, (B) 30 hr, (C) 80 hr, and (D) 100 hr.

little further change in activity was observed.

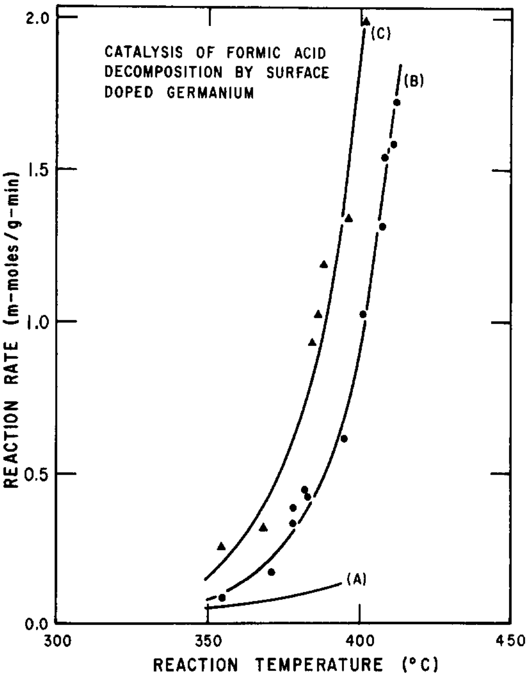

Fig. 4. Decomposition of formic acid over germanium samples doped from the vapor phase by gallium. Source temperature is 400°C the diffusion temperature 800°C. Curve (A) no doping; (B) 2 hr diffusion, (C) 4 hr diffusion. This treatment yields germanium doped to the solubility limit.

Figure 4 shows the variations of reaction rate with temperature for samples doped *p*-type with gallium vapors. In this case a 2-hr diffusion at 800°C gave the activity level attained by annealing in Pyrex for 30 hr. The 4-hr gallium diffusion period is roughly equivalent to the 100-hr Pyrex annealing period. These diffusions were accomplished using gallium from a gallium source at 400°C. In these experiments product gases were analyzed by gas chromatography. Only carbon monoxide was detected; thus, only the dehydrogenation appears to be influenced by the doping. In the work of Moore (*4*) only this reaction was affected by changes in doping concentration.

Discussion

Activities induced in germanium by *p*-type bulk and surface doping indicate that surface doping is far more effective. Teichner and Aigueperse suggest, for ethylene hydrogenation over zinc oxide, that the presence of excess zinc at the oxide surface is the determining factor and that electronic conductivity is of no significance. However, the excess zinc at the surface constitutes a doped oxide surface. The only question is: Why could this effect not be reproduced in the bulk by hetero-ions? The situation is closely analogous to the case of formic acid decomposition over germanium. *p*-Type doping at the surface is effective catalytically, but *p*-type bulk doping is not. In the case of germanium, however, techniques for achieving these different types of doping are different: Bulk doping is done by the traveling zone or the pulled crystal technique, while surface doping is done by condensing the dopant from the vapor. Both bulk-doping techniques depend on the liquid–solid segregation coefficient and are limited in the achievable concentrations by constitutional supercooling (*8*). The doping level achievable in a crystal using the vapor is limited only by the solubility of the dopant in the host crystal. This technique is capable of dopant concentrations of 5×10^{20} carriers/cm^3, while the other techniques can achieve a maximum of only about 10^{20} carriers/cm^3.

Thus, for germanium at least, there is an assignable electronic difference between material which has been bulk-doped and surface-doped. The latter doping is greater. There are two likely explanations why these large carrier concentrations are necessary for catalytic activity.

First, at temperatures providing high rates of formic acid decomposition, germanium is intrinsic (i.e., there are equal numbers of holes and electrons) for all but very high dopant concentrations. Doping concentration must be very large before any activity appears other than that associated with undoped germanium.

At 300°C, material doped to 2×10^{17} or less is intrinsic and exhibits a resistivity of about 0.03 ohm-cm. In the temperature region of the present work (300–400°C) carrier density must exceed 10^{19} carriers/cm^3 for the sample to exhibit greater than intrinsic conductivity. Moore, Smith, and Taylor had only one sample in which this carrier density was achieved. The activity measured for this sample compares well with the activity measured for a sample annealed 100 hr in the presence of Pyrex in the present work.

Another effect which can obscure any activation due to bulk doping has been discussed by Garrett (*9*). This is the case where there is a high concentration of adsorbate on the surface. In this case, the surface carrier density resulting from charge-transfer adsorption is greater than can be achieved by carrier transport from the bulk. The only way to overcome this condition and again assert the effect of the catalyst on the reaction is to increase the concentration of dopant and consequently increase the surface concentration of carriers. However, our work with highly doped semiconductor materials indicates that bulk doping cannot provide such increases in carrier density. It appears that vapor-phase doping is the only way to increase surface carrier concentrations to a level where the catalyst again controls the reaction on the surface.

It may be that the H_2-D_2 exchange exhibits changes in activity at lower carrier concentrations than does formic acid decomposition for just such a reason as the above. It seems plausible that the adsorption of formic acid should be stronger than that of hydrogen. There would be a greater amount of electron transfer to compensate and a greater carrier concentration would be required for the more strongly adsorbed species.

CONCLUSIONS

(1) When possibilities for surface doping a germanium catalyst are excluded, the decomposition of formic acid over the catalyst is little affected by changes in bulk concentrations of carriers. In the present work varying bulk concentration by two orders of magnitude has no measurable effect on the reaction rate.

(2) Pyrex glass in a system at 600°C can serve as a source of *p*-type dopant for germanium. Gradual doping of the surface by boron from the Pyrex during successive anneals gradually increases the activity of the catalyst.

(3) High values of activity and surface concentration of holes can be quickly obtained by vapor-phase doping of the germanium surface using a gallium source at 400°C and holding the germanium at 800°C.

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