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Catalytic and Chemical Reaction Rates of Hydrogen Atoms with Germanium*

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The catalytic and chemical reaction rates of hydrogen atoms with germanium were determined for single crystals of three doping levels. The catalytic rate constant for the heterogeneous atom recombination was found to be 1.6×10^4 cm $\sec^{-1}$. This rate is larger by a factor of 10^4 than the rate of the chemical reaction which results in a volatile germanium hydride and tends to keep the surface clean. Neither reaction rate depends upon the doping level, and the probable reasons for this lack of dependence are discussed. The experimentally determined hydrogen atom recombination coefficient on germanium, i.e., the catalytic reaction, was found to be in agreement with the value predicted for metals on the basis of the solid's Debye temperature.

INTRODUCTION

This investigation, part of a program on the interactions between gaseous atoms and solid surfaces, seeks to determine whether the chemical and catalytic reactions between hydrogen atoms and the semiconductor germanium depend upon the bulk electronic properties of the solid, and whether the catalytic rates can be correlated, as for metals (*1*), with the solid's Debye characteristic temperature.

Germanium is particularly well suited for studying the effect of bulk electronic properties upon catalysis, because single crystals of high purity are available, and the bulk electronic properties can be varied widely by small concentrations of dopants. The germanium–hydrogen atom system seemed particularly attractive for a study of surface reactivity because the process of volatile hydride formation should clean the surface continuously. Indeed, a field-emission microscopy study of germanium has demonstrated that the most successful cleaning technique is a field-induced etching reaction between hydrogen (atoms) and germanium (*2*).

Chemically doped germanium has been used in a number of similar studies which are summarized in Ref. (*3*). In some of these studies marked differences in catalytic reaction rates were found between *n*- and *p*-type samples, although the degree of doping was often without influence. In only one of several studies of the H_2–D_2 exchange on a germanium surface was a dependence of activity upon extent of doping found.

In the present investigation two reactions with gaseous hydrogen atoms were explored: the catalytic recombination of hydrogen atoms on the semiconductor surface, S,

$$H + H\text{--}S \xrightarrow{k_1} H_2 + S$$

and the chemical reaction in which a volatile germanium hydride* GeH_x is produced

$$xH + Ge \xrightarrow{k_2} GeH_x$$

THE CATALYTIC RECOMBINATION OF HYDROGEN ATOMS

Experimental

The catalytic recombination of hydrogen atoms on germanium single-crystal wafers

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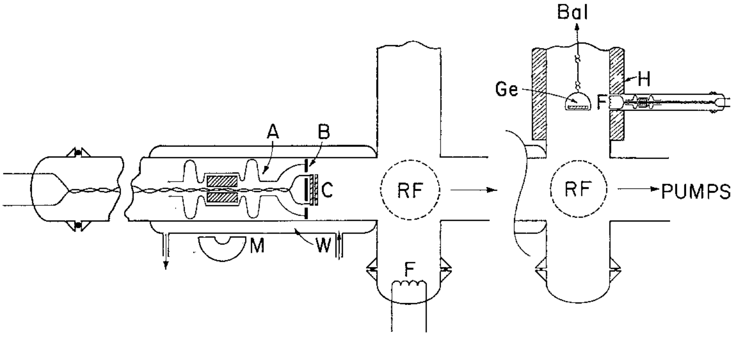
* The stoichiometric composition of the hydride has not been identified as yet.

was investigated by a modified microcalorimetric method (*4*). The semiconductor wafer was exposed to hydrogen atoms diffusing along a cylindrical glass tube, and the atom concentration was measured at various positions from the atom source. The microcalorimeter [see Fig. 1(a)] was composed of a base plate of intrinsic† germanium (16 × 16 × 0.5 mm). Two copper leads were soldered to the back of the crystal on opposite sides near the edge. Germanium crystals (Eagle-Picher Co. and General Diode Co.) of various dopings were fastened by Sauereisen cement to the base plate, and a sheet of mica (0.01 mm thick) provided electrical insulation between the two plates without appreciably reducing thermal conduction. Sauereisen cement was also applied in a thin layer to the back surfaces of the calorimeter and test specimen. The semiconductor crystals were 0.020 inch thick and either square (16 × 16 mm) or circular (25-mm diameter). The calorimeter was heated electrically by Joule heating to a given temperature (resistance) which was indicated by a DC bridge. The negative temperature coefficient of resistance of germanium requires a constant current source.

The hydrogen atoms were generated by an electrodeless radiofrequency discharge from an 18-Mc/sec, 500-W transmitter; the atom density was monitored with a tungsten filament. The discharge was pulsed ("On" 1 sec and "Off" 30 sec), and the small rise in calorimeter temperature, which was indicated by the imbalance of the bridge, was proportional to the atom density. The unbalanced bridge current was detected by a microvoltameter which served as a buffer amplifier (with a constant impedance to the bridge) to provide the voltage equivalent of the bridge imbalance to a microvoltmeter. The maximum deflection of the microvoltmeter (~3 sec) was used as a measure of the atom density.



(a) (b)

FIG. 1. Schematic drawing of apparatus for measurement of catalytic and chemical rates. Symbols: A, assembly; B, glass baffle disk; C, germanium calorimeter; Ge, germanium crystal; Bal, Cahn electrobalance; F, tungsten filament; M, magnet; W, water-jacketed cylinder; and RF, rf frequency excitation of H_2 (in arm perpendicular to paper).

This pulse technique was rapid and reproducible. Its response was linear with both pulse duration (0.5 to 10 sec) and atom density (over range of available radio frequency power). Also the values of γ' so obtained agreed with those determined by the usual steady state calorimetric technique (*4*). The pulse method was particularly useful in the case of germanium because the reaction products with hydrogen atoms, over the long periods of exposure required for the steady state measurement, caused the catalytic activity of the glass walls to increase.

The germanium surfaces to be exposed to atoms were etched (10% HF in HNO_3 1–3 sec) then rinsed with water without removal from the etch solution. Prior to the measure-

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† Intrinsic germanium is used because its temperature–resistance properties are more favorable than doped crystals.

ments and in order to "clean" a crystal surface, a given crystal was exposed to a high hydrogen atom density close to the source for periods of up to 18 hr; however, within the limit of error, the recombination of hydrogen atoms remained unaffected by this pretreatment. The measurements were made at a hydrogen pressure of 0.10 Torr and with a hydrogen atom density of about 2×10^{14} atoms/cm^3 at the source.

Before measurements were made, the system was evacuated to a residual pressure of about 2×10^{-6} Torr. During measurements the pressure was adjusted by the flow rate of hydrogen, purified by diffusion through palladium.

The results were evaluated according to the analysis by Wise and Ablow (*5*), and the atom recombination coefficient γ' was determined as the ratio of recombined hydrogen atoms to the total number of hydrogen atoms striking the sample surface. It was corrected (*6*) for the area of the crystal according to the expression $\gamma' = \gamma'_a(a_0/a)$, where γ'_a is the recombination coefficient obtained for the crystal of area a, and a_0 is the cross-sectional area of the cylinder.

Results and Discussion

The value of γ' for germanium was determined for crystals of three different doping levels: n-type (2×10^{18} As/cm^3), n-type ($\sim 3 \times 10^{13}$/cm^3), and p-type (3×10^{18} Ga/cm^3), and at least six determinations were made for each crystal. The value of γ' at 90°C was found to be 0.25 ± 0.06, and was essentially independent of the atom density in the gas (i.e., the reaction is first order with respect to atom density in the gas), and also independent of doping level. A change in geometric area of the germanium from 2.5 to 5.0 cm^2 caused no change in γ', within the limits of error, in accordance with the theoretical corrections applied for area of the sample probe (*6*). The catalytic rate constant, k_1, calculated (*5*) from this value of γ' and from the hydrogen density measured by an auxiliary tungsten filament calorimeter is $1.6\ (\pm 0.4) \times 10^4$ cm sec^{-1}.

As the germanium temperature was increased from 90° to 170°C the value of γ' increased about 50% (activation energy of 1 to 2 kcal/mole). The temperature difference between the germanium probe and the gas is not sufficiently large to attribute this effect to changes in diffusional transport of atomic hydrogen (*1*).

Preliminary measurements of γ' for hydrogen atom recombination on silicon (etched with concentrated HF then flushed with methanol) also showed no dependence on doping level, with samples doped from 10^{20}/cm^3 p-type to 10^{20}/cm^3 n-type. The surface composition of the silicon may not be as well defined as that of germanium because of the absence of volatile hydride formation in the case of silicon.

The recombination coefficient of the glass walls for hydrogen atoms was evaluated as part of the above analyses and found to be $3(\pm 1) \times 10^{-3}$ in agreement with published values (*7*).

THE CHEMICAL REACTION

Experimental

The chemical reaction of germanium with hydrogen atoms was studied by measuring the rate of weight loss of a germanium crystal (area $\sim$0.3 cm^2 and 0.5 mm thick) suspended from a Cahn recording microbalance and exposed to hydrogen atoms. The vacuum apparatus is shown in Fig. 1(b).

Measurements were made on the germanium crystals (lapped by the supplier) after cleaning in benzene and acetone, and then on some of the same crystals after etching (10% HF in HNO_3 for 1 min) and rinsing in deionized water. The etch treatment was intended primarily to remove surface impurities, and also to reduce the effect of dislocations resulting from lapping. Some of the etched crystals were then lapped with O-grade emery paper, in an attempt to reproduce the condition (e.g., dislocations) of the original samples.

The effect of temperature on the chemical reaction of a lapped sample was studied by heating the tube containing the suspended germanium sample. The temperature was measured by a thermocouple inside the vacuum apparatus and close to the sample, and the atom density was measured with a tungsten filament, contained in a small diameter sidearm, which could be magnetically moved close to the sample.

Results and Discussion

The reaction rate constant of the chemical reaction, k_2, is determined by

$$-dw/dt = k_2 n$$

where $-dw/dt$ is the rate of weight loss per cm^2 of the germanium and n is the hydrogen atom density at the sample surface.

For a given germanium sample and for conditions of constant pressure and hydrogen atom density, the chemical rate remained constant over the period of observation (up to 24 hr), except that somewhat higher rates were observed during the initial period of 10–15 min. The initial period probably represented temperature equilibration of the discharge and/or removal of residual surface oxide. The succeeding constant chemical rate amounted to several atomic layers of Ge per min.

Measurements were made on germanium crystals at six doping levels ranging from n-type (2×10^{13} As/cm^3) to p-type (5×10^{17} Ga/cm^3). The chemical reaction was found to be first order with respect to the hydrogen atom density in the gas.

At 25°C the reaction rate constant k_2 is 1.4 ± 0.2 cm/sec, and these values are independent of doping level for the etched and the subsequently lapped germanium crystals.

However threefold greater values were obtained in the initial measurements (i.e., lapped crystals as supplied and solvent-cleaned) for two extreme n-type dopings. Since the surfaces of these samples are probably more likely to be contaminated than those of the etched samples, it was of interest to explore the nature of the impurity and the mechanism by which the chemical rate was enhanced for the extreme n-type germanium. A likely contaminant is copper, which in extremely small quantities can profoundly affect the surface states of germanium (*8*). The effect of Cu was studied in the following experiment: An etched germanium crystal, p-type ($\sim 3 \times 10^{13}$ cm^{-2}), was immersed 1 min in 1 ppm $Cu(NO_3)_2$ solution and rinsed, a condition which may be expected to produce 10^{11} to 10^{12} globules/cm^2 of Cu about 100 Å in diameter (*8*). Controlled copper contamination, however, resulted in a decrease in the reaction rate by a factor of 2. Therefore, it is unlikely that the threefold greater reaction rate can be accounted for by copper contamination. Nor is it likely that the greater rate can be accounted for on the basis of surface dislocation density since the rate was unaffected by lapping subsequent to the etching.

The reaction rate of a lapped n-type germanium sample (2×10^{18} As/cm^2) was found to decrease with increasing temperature. Rate constants, calculated for atom concentrations as actually measured by the tungsten filament in the sidearm, varied from a value of 1.4 to 0.5 cm sec^{-1}, as the temperature was raised from 25° to 235°C. The decrease in reaction rate may be partially due to an increased rate of the backward reaction, i.e., decomposition of product on the germanium surface. However, the rate of decomposition of GeH_4 (*9*), a possible reaction product in our experiments, is probably too slow to account for this temperature effect.

In a comparable experiment a silicon crystal exposed to hydrogen atoms encountered no detectable weight loss.

CONCLUSIONS

For germanium the reaction rate constant for the catalytic atom recombination is greater by a factor of about 10^4 than for the chemical reaction. The determination of γ' is therefore not significantly affected by the heat generated due to the chemical reaction. It is probable that the volatile hydride formation maintains the germanium surface substantially free of impurities such as oxides.

It is of interest to determine how the above results for germanium fit the correlation found for metals (*1*) between the Debye temperature of the solid, θ_D, and the hydrogen atom recombination coefficient γ'. This correlation is based on the postulate that those solids which exhibit higher velocities of propagation of the longitudinal and transverse waves, as indicated by θ_D, will be more readily able to dissipate the energy released in the heterogeneous reaction and thus will have higher values of γ'. According to this correlation, the value of θ_D for germanium is reported to be about 400 (*10*), and leads to a γ' of 0.2. Thus the measured value for germanium is in agreement with the correlation.

It is concluded that bulk electronic properties of germanium, and probably also of silicon, do not appreciably affect either the catalytic properties for hydrogen atom recombination or the chemical properties for volatile hydride formation. The absence of the effect of bulk electronic properties could be accounted for if (1) the binding energy (surface states) of the adsorbed hydrogen atoms, which enter into the mechanism of the two reactions, is not appreciably affected by the electronic bulk properties of the solid, (2) the Fermi energy for all doping concentrations used is "pinned" by surface states due either to Tamm states (*11*) or to adsorbed hydrogen, or (3) the rate-limiting step of the catalytic recombination reaction is related to the energy accommodation by the solid, as in the Debye temperature formulation, and not to the chemical or electronic form of the adsorbed species. The dopant concentrations we used with germanium were lower than those (in the range of 0.01%) required for an observable effect on the H_2–D_2 exchange (*3*). At higher dopant concentration it is possible that influences unrelated to the bulk electronic properties may dominate.

The calorimetric technique developed for this study promises to be useful to study the catalytic properties of various materials which can be applied (as single-crystal wafers, evaporated films, foils, or cemented powders) to the face of the germanium calorimeter and which otherwise would be difficult or inconvenient to fabricate as filaments.

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