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Electrolytic Etching at Small-Angle Grain Boundaries in Germanium

S. G. ELLIS
RCA Laboratories, Princeton, New Jersey

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There is a difference of appearance between *n*-type and *p*-type germanium crystals which have been anodically etched. This can be explained if only the hole current contributes to the etching. An *n*-type crystal can be made to etch in the same way as a *p*-type crystal if injected holes reach the crystal-electrolyte interface. Hole-electron recombination within the crystal can then reduce the rate of etching. Such recombination at small-angle grain boundaries has been demonstrated.

THE distribution of current in a piece of germanium which is being anodically etched will depend in part on the distribution of potential at the surface of the germanium and in part on the variation of the electronic properties (conductivity and lifetime) within the germanium. It might therefore be expected that the shape of the etched surface would reflect in some degree any inhomogeneities within the crystal. An effect of this sort has been found. It demonstrates carrier recombination at dislocations in germanium. It is desirable, for clarity, to preface a description of this effect with an account of some of the general features of the electrolytic etching of germanium.

If a *p*-type germanium crystal is electrolytically etched in a potassium hydroxide solution from a macroscopic viewpoint the removal of material is uniform over the immersed area. At current densities of a few microamperes per cm^2 the microscopic appearance of the surface is similar to, but not identical with, that of a crystal treated with an alkaline chemical etch.[1] The attack during electrolysis is nucleated where dislocations end at the surface, leading to pit formation at such places. These pits are shallow, seldom exceeding a micron in depth. As the current density is raised, the surface becomes smoother. Electropolishing occurs at current densities of the order of an ampere per cm^2.

With *n*-type germanium, the attack is quite different if the electrical connection to the crystal is many diffusion lengths away from the crystal-electrolyte interface. (Diffusion length here refers to the diffusion length of minority carriers in the germanium.) Under such conditions a few deep widely-spaced pits are produced, and there seems to be very little, if any, reaction at other points on the surface. The pit depth depends on the charge passed. When the pits are deep a product of the reaction forms within them. It is probably a hydrated form of germanium monoxide. It has been suggested[2] that the deep pits are formed because the monoxide attacks the germanium so that the reaction is self-catalytic. The observations with *p*-type germanium make this explanation improbable.

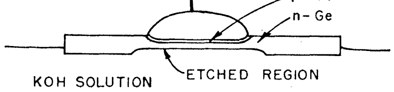

FIG. 1. Etching of a thin *n*-type Ge crystal.

The current-voltage curves for crystals being etched under such conditions[3] indicate that a junction exists at or near the germanium-electrolyte interface. When a *p*-type crystal is being etched the current passes in the forward direction, while with an *n*-type crystal the etching current is in the back direction. The deep pitting with *n*-type crystals can be explained if it is supposed that the junction breaks down at a few places so that the current and hence the etching is localized.

If an injecting contact is made to an *n*-type crystal, thin compared with a diffusion length (Fig. 1), the current in the germanium will consist chiefly of holes. Under these conditions etching takes place evenly on a macroscopic scale, as for a *p*-type crystal. The etching is apparent only where the holes reach the germanium-electrolyte surface. An interesting effect is observed if a small-angle grain boundary runs through the etched region. Near such a boundary the etching is *less* rapid than elsewhere. See Fig. 2.

This observation can be explained by supposing that the dislocations which form the small-angle grain boundary are the sites of traps which permit hole-electron recombination.[4] The hole current which reaches

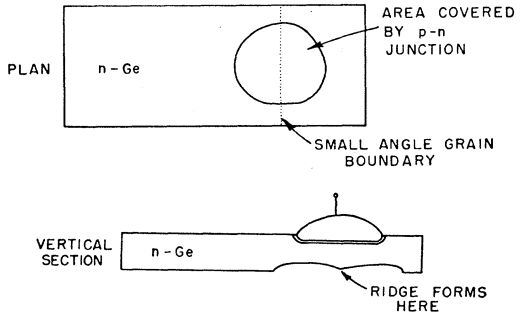

FIG. 2. Effect on etching when a small-angle grain boundary runs through the etched region of a thin *n*-type Ge crystal.

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the germanium-electrolyte interface near the small-angle grain boundary is therefore reduced and the etching consequently retarded.

The dislocations in such boundaries are commonly of the order of 10^{-4} cm apart. Etching studies[1] show that dislocations of a different character are scattered throughout the crystal with a similar (3-micron) inter-dislocation spacing. The above observation shows, therefore, that not all the dislocations are equally effective as recombination centers. Such observations do not show whether the dislocations are themselves the recombination centers or merely the preferred sites for impurity atoms which behave as recombination centers.

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Magnetic Susceptibility of Sodium Metal

RAYMOND BOWERS
Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania

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The total susceptibility of sodium metal has been measured from room temperature down to 55°K using the Gouy technique. The mass susceptibility at room temperature was found to be $+(0.70\pm0.03)\times10^{-6}$ cgs units. This result is analyzed by using an estimate of the ion core susceptibility and calculations of the conduction-electron spin contribution. The analysis leads to a conduction-electron orbital diamagnetism which is much smaller than the value obtained from the Landau-Peierls formula. No explanation is given of this disparity.

The susceptibility decreases by 4.5% between room temperature and 55°K. No abnormal behavior was found in the susceptibility between 77°K and 55°K where the Knight shift exhibits an anomaly. An account is given of experimental difficulties which were encountered in an attempt to measure the susceptibility at liquid helium temperatures.

INTRODUCTION

THE total magnetic susceptibility χ of metallic sodium is the sum of three components, namely, the diamagnetism of the core electrons χ_c, the paramagnetism due to the spin of the conduction electrons[1] χ_s, and the diamagnetism due to the orbital motion of the conduction electrons[2] χ_0. In this paper we shall be interested in the magnitude of these components.

For simple metals such as sodium, the contribution due to the core can be determined indirectly from the measured susceptibility of sodium salts[3] and can also be calculated with reasonable confidence using Hartree-Fock wave functions.[4] The determination of the two conduction-electron contributions, particularly the orbital component, is much more difficult. The free-electron calculations, while giving a qualitative understanding of why the susceptibility is almost temperature-independent, are not satisfactory quantitatively. The susceptibility of sodium computed on the basis of the free-electron model[5] leads to a value which is too low by a factor of 3.

A number of recent developments have renewed interest in the susceptibility of sodium metal, particularly concerning the determination of the component susceptibilities. First, an experimental technique has been developed for measuring the spin contribution directly.[6] Only lithium has been studied so far but measurements on sodium are being made currently. Secondly, new theoretical values have been published for the spin contribution. Pines[7] has applied the Bohm and Pines collective-electron theory to this problem. Furthermore, calculations have been made by Townes, Herring and Knight[8] and by Kohn and Kjeldaas[9] of the spin contribution from the experimental value of the Knight shift in sodium.

With the value of ion core susceptibility and these recent values for the spin contribution, an estimate of the orbital contribution can be obtained if the total static susceptibility is known. Since there is a wide scatter in the published data,[10] we have redetermined this total susceptibility.

Apart from the absolute value of the susceptibility at room temperature, we have measured the suscepti-

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