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New Annealing Effects on the Bulk Corrosion Potential of Germanium

Abstract: The corrosion potential (U_k) of n-type Ge with donor concentrations less than 10^{18} cm^{-3} was drastically changed ("ΔU_k effect") by heat treatments between 600 and 800 °C. The formation of recombination centers due to Cu contamination is probably the principal cause.

Introduction

The corrosion potential, U_k, of n-type Ge electrodes immersed in appropriate aqueous solutions depends strongly on the donor concentration present.[1–3] Thus U_k can be used to monitor impurity profiles[2,4] in bulk, diffused, or epitaxial n-type Ge layers. In studies of this measurement technique it was observed that U_k of n-type Ge, having donor concentrations of less than 10^{18} cm^{-3}, can be drastically changed by heat treatment at temperatures between 600 and 800 °C. This communication reports investigations of this new effect which is hereafter referred to as the "ΔU_k effect."

Experimental results

The solid curve in Fig. 1 shows previously published U_k measurements.[2,3] The corrosion potential of polished[5] Ge samples was measured potentiometrically referenced to a saturated calomel electrode. The electrolyte consisted of 0.1M $K_3[Fe(CN)_6]$, 0.1N NaOH, and 1.0N $NaNO_3$. The dashed lines in Fig. 1 illustrate how the U_k curve shifts if the measurements are carried out on samples which were previously heat treated for 100 min in forming gas (90% N_2 and 10% H_2) at 600, 700, and 800 °C, respectively. No changes in U_k were observed with p-type and heavily doped n-type wafers subjected to the same heat treatments.

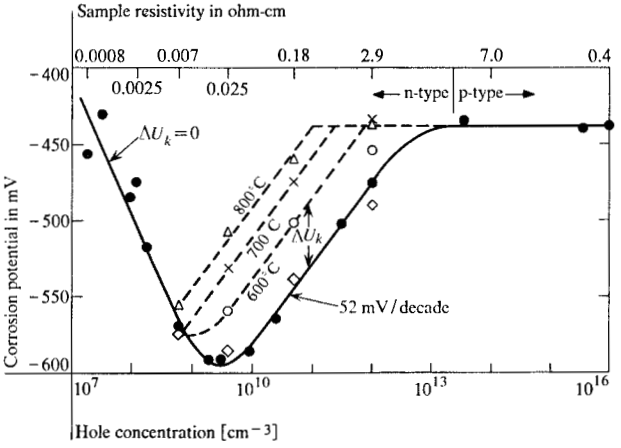

Figure 1 Corrosion potential (U_k) of Ge vs. hole concentration. The solid curve refers to U_k measurements[2,3] before, and the dashed lines to U_k measurements after, 100 min forming-gas treatment at 600, 700, and 800 °C. The open squares represent data subsequent to that of Refs. 2 and 3.

• *Forming-gas annealing*

Figure 2 presents details of the ΔU_k effect observed on an n-type sample with resistivity of 0.025 Ω-cm. Here ΔU_k is plotted vs. the annealing time in forming gas. Corresponding results have been obtained with 0.18 Ω-cm, n-type samples. The U_k measurements following the heat treatments were carried out after 2 mils of surface layer had been removed. All measured ΔU_k values represent, therefore, a true bulk effect. Another feature to be noted is that ΔU_k was only a function of temperature when annealing times in excess of 40 min were employed. On the other hand, heat treatments between 400 and 500 °C did not alter U_k at all. Repetition of the forming-gas experiments in vacuum, H_2, He, Ar, dry N_2, and wet N_2 yielded the same results.

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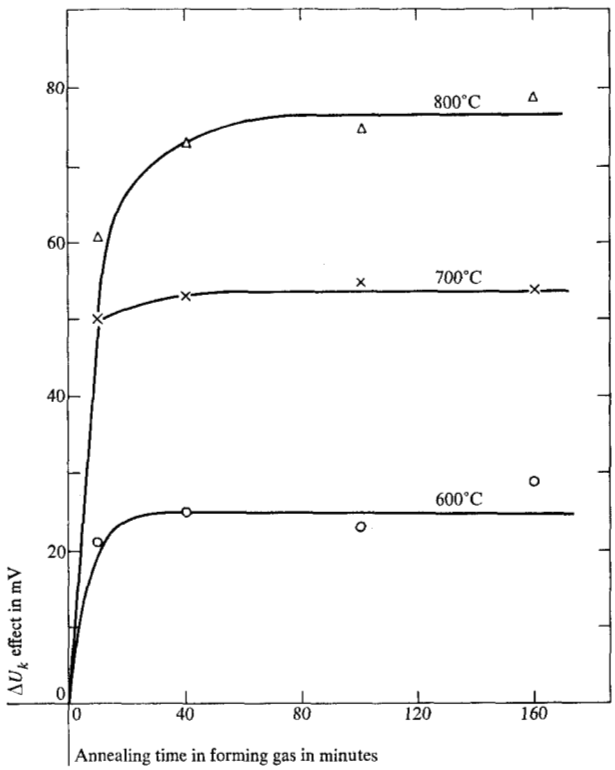

Figure 2 The ΔU_k effect observed in 0.025 Ω-cm, n-type Ge after forming-gas treatments for periods up to 160 min; ΔU_k remained constant during heat treatments of 64 h.

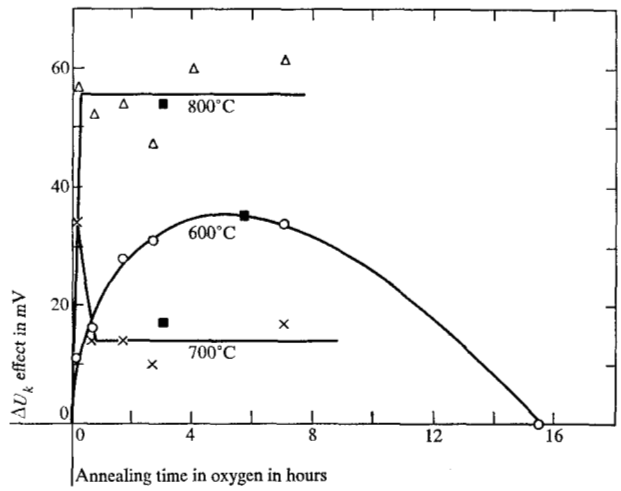

Figure 3 The ΔU_k effect observed in 0.025 Ω-cm, n-type Ge after oxygen treatments for periods up to 15.5 h. The solid squares represent samples which received a pre-bake in H_2 for 100 min at 800 °C.

No change in the resistivity could be detected at room temperature in the heat-treated 0.025 and 0.18 Ω-cm samples. The resistivity of lightly doped, n-type samples, however, had changed after the 600 °C forming-gas treatments from 2.9 to 4 Ω-cm. Perhaps even more significant was the observation that heat treatments in forming gas at 700 or 800 °C converted the conductivity type of this 2.9 Ω-cm sample from n- to p-type.

• *Oxygen annealing*

The ΔU_k effect exhibited a complicated time-temperature dependence when the heat treatments were carried out in oxygen. Data for the 0.025 Ω-cm, n-type samples are presented in Fig. 3 as a function of the annealing time in O_2. Again it was found that the ΔU_k effect is a bulk effect and that it is not accompanied by a measurable change in the room-temperature resistivity of the Ge wafers. A pre-bake in hydrogen at 800 °C for 100 min prior to an O_2 treatment did not modify the ΔU_k changes following the O_2 treatment. The ΔU_k value at each annealing temperature for such sequential gas treatments is denoted by a full square. Two major differences are apparent in Fig. 3 compared to the ΔU_k results seen after forming-gas treatments: (1) The value of ΔU_k can be larger at 600 °C than at 700 °C and (2) the ΔU_k curve for 600 °C reaches a maximum for an annealing time of approximately 5 h.

Discussion

The marked difference in the temperature dependence of the ΔU_k effect after oxygen and forming-gas treatments, respectively, is also reflected in the appearance of the heat-treated wafer surfaces. The forming-gas exposures leave the polished surfaces unchanged while the 600 °C O_2 treatments cover the polished Ge surface with an oxide film that increases in thickness with increase in annealing time. At 700 °C the O_2-treated wafers are covered with a clean surface film,[6] the appearance of which does not change with annealing time. The 800 °C O_2 treatments result in heavy thermal etching of the Ge wafers. Therefore 5 to 6 mils of surface had to be removed after the O_2 treatments before reliable U_k measurements could be made in the absence of surface damage.

The observation of a bulk ΔU_k effect and its time-temperature dependence rules out the possibility that the effect is caused by the diffusion of gas molecules* or substitutional impurities. The unchanged resistivity represents further evidence that the ΔU_k effect cannot be explained on the basis of a doping process.

Gerischer and Beck[1] have presented a model which explains U_k of n-type Ge on the basis of a quasi-photovoltaic

* The diffusion constant of H_2 in Ge[7] would certainly be large enough in the temperature interval in question to account for a bulk effect; however, Ge is nearly impermeable to N_2 and Ar[7] and in these ambients the same ΔU_k effect was found. Furthermore, the diffusion constant of O_2 in Ge[8] is much too small to cause an O_2 penetration depth of 5 to 6 mils within an annealing time of only a few hours.

effect. They found that the difference between U_k of p-type and n-type Ge becomes smaller if either more holes and/or more recombination centers are present in the n-type samples. This suggests that the ΔU_k effect might be attributable to the formation of recombination centers, the probability of a doping effect having been shown to be low. A similar argument had been employed by Weiser[9] to discuss the effect of annealing on the bulk lifetime of Ge. The present observation that the 2.9 Ω-cm, n-type sample converted to p-type after 700 or 800 °C heat treatment indicates the possibility that Cu contamination could cause the ΔU_k effect. In fact, the ΔU_k effect of 0.02 Ω-cm, n-type samples was always either much less pronounced or not visible at all if the samples were treated in a KCN solution prior to the annealing experiments to remove Cu from the wafer surfaces.[10] The ΔU_k effect of a deliberately Cu-contaminated sample was approximately the same as previously seen with regular n-type samples.

Based on the above evidence, we propose that Cu, acting as a recombination center,[11] is the major origin for the ΔU_k effect. The temperature dependence of the ΔU_k effect in forming gas could then be correlated to the temperature dependence of the solubility of Cu in Ge.[11–13] In the case of the O_2 treatments, one has to distinguish between the low- and high-temperature processes. The oxide layers formed at 600 and 700 °C may act as a "getter" for the Cu impurities. Consequently an O_2 treatment of a 2.9 Ω-cm, n-type wafer at 700 °C for 100 min should not convert its conductivity type; this was verified experimentally. The 800 °C O_2 treatment is somewhat similar to the corresponding forming-gas treatment. The thermal etching during the O_2 run reduces the Cu concentration by either the etching process itself or by a chemical transport reaction involving O_2. Therefore ΔU_k becomes smaller in magnitude than the value observed after forming-gas treatments.

More vigorous gettering experiments, during which Cu is totally extracted from the Ge material, should demonstrate quantitatively what fraction of the ΔU_k effect is truly attributable to Cu contamination. Besides its importance for the practical application of the corrosion-potential method for measuring impurity profiles, the ΔU_k effect might also become a simple but very sensitive tool for detecting electrically inactive impurities in Ge.

Acknowledgments

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