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ABSTRACT

A method for copper staining germanium crystals is described. This method can be used to show nonuniformities in germanium crystals prior to Li drifting, and as a tool for studying the diffusion and drifting of Li in germanium.

I. INTRODUCTION

Techniques capable of showing junctions and impurity inhomogeneities in semiconductor crystals constitute an important tool in device fabrication and development. Copper staining by white light illumination of a sample immersed in a Cu^{++} solution has been used as a tool to decorate Si crystals^{1,2)}. However, to our knowledge, the decoration of Ge devices could be accomplished only through various adaptations of techniques based upon preferential chemical etching and electrolytic plating³⁾. This report describes how to provide excellent decoration of Ge crystals by copper staining.

II. DESCRIPTION

The key conditions for proper decoration of Ge crystals by copper staining are:

- a) Low solution temperature $\sim 3^{\circ}\text{C}$.
- b) Illumination of the sample by infrared light.
- c) Careful positioning of the light source relative to the germanium sample so to minimize the absorption of the infrared light.

The staining solution used throughout this work contained 20 gr $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 1 cc 48% HF per liter of solution. Ten fold variation in CuSO_4 and HF concentration showed no significant effect on the quality of the stain. The concentration used is identical to the one previously reported for the staining of $\text{Si}^{(4)}$.

The solution must be kept at temperature near the freezing point to obtain clear stains. As the temperature is increased to $> 10^{\circ}\text{C}$ the stains on the p-i-n junctions of a device become fuzzy; at room temperature a lack of contrast, especially between the p-i regions, makes the stain unusable. A brief investigation with solutions containing methanol and ethylene glycol indicated that at -25°C only the n region is clearly visible even after doubling the normal exposure time. Complete stains of the p-i-n junctions are observable when the temperature reaches $\geq -10^{\circ}\text{C}$. A water solution cooled to around 3°C was used to obtain the stains reported in this letter.

The use of light is essential in copper staining since the method is based on a photovoltaic effect causing more electrons to accumulate on n type material, and therefore preferential plating of the Cu^{++} ions³⁾. By comparison, the i region on which more electrons accumulate than on the p region, but less than on the n region will be plated accordingly. Most distinct region separation has been obtained with the use of an infrared lamp. Since infrared radiation is absorbed by the Cu^{++} solution, the sample is irradiated through the glass bottom of the dish and therefore through the sample rather than through the top of the solution.

A diagram of the apparatus utilized is presented in Fig. 1. The surface to be stained is carefully lapped and dried with a jet of dry nitrogen. The sample is then immersed in the solution kept at $\sim 3^{\circ}\text{C}$ by an ethylene glycol cooling coil. After a 30 sec delay the infrared light is turned on for a period of 2 to 4 minutes depending upon the size of the sample. The liquid nitrogen cooled collimator allows longer exposure if desired without causing a serious temperature rise of the staining bath. During the staining exposure a 0.3 liter/min flow of Ar is bubbled into the bath to provide a stirring action without which the presence of heat currents rising from the faces of the device will cause severe distortion of the stain. A piece of copper pipe is located in the bath to promote a circular motion of the solution.

Figure 2 shows a stain on a typical Li drifted germanium crystal. The diffused, drifted and uncompensated regions are clearly decorated with sharp separation at the junctions. The picture of the stain

is taken under light shining at a grazing angle to allow for maximum contrast. The sharpness of the boundaries illustrates the usefulness of the method as a tool to investigate the shape and depth of all three regions.

The method is sufficiently sensitive to show nonuniformities in germanium crystals prior to Li drifting. In the fabrication of radiation detectors a uniform drifted region must be achieved. Figure 3 presents the spiraling pattern of a stain observed of Ge crystals from which nonuniform drifted regions were obtained. The spot pattern shown in Fig. 4 was observed on crystals from which detectors of high trapping characteristics were fabricated. The best detectors from the point of view of good resolution and low trapping have been made from materials exhibiting very uniform copper deposition when stained prior to lithium drifting. Therefore, as with our groups observation previously using copper staining on silicon, the technique can be used to weed out poor quality crystals without requiring the elaborate process of lithium drifting. The better crystals must still be graded by testing detectors however.

ACKNOWLEDGMENT

The author is grateful for the help of G. Saucedo in the building of the apparatus. Valuable contributions to development of the technique and its application have been made by W. Hansen, R. Pehl and F. Goulding.

FOOTNOTE AND REFERENCES

*Work done under the auspices of the U. S. Atomic Energy Commission.

- 1) P. J. Whoriskey, J. Appl. Phys. 29 (1958) 867.
- 2) P. A. Iles and P. J. Coppen, J. Appl. Phys. 29 (1958) 1514.
- 3) P. J. Holmes, The Electrochemistry of Semiconductors (Academic Press, London and New York, 1962) Chapters 6, 7 and 8.
- 4) R. P. Lothrop and H. E. Smith, Lithium-Drifted Silicon Radiation Detector Production Process, Lawrence Radiation Laboratory Report UCRL-16190, June 1965.

FIGURE CAPTIONS

Fig. 1. Cut-away view of the staining apparatus

Fig. 2. The p-i-n regions of a Li drifted Ge detector.

Fig. 3. Stain of a Ge crystal from which a highly non-uniform drifted region was obtained.

Fig. 4. Stain of a Ge crystal from which detectors of high trapping characteristics were fabricated. The spot pattern is visible in the center of the device.

XBL 688-5655

Fig. 1

XBB 688-4906

Fig. 2

XBB 688-4905

Fig. 3

XBB 688-4907

Fig. 4

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