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IMAGING AND ANALYSIS OF CARBON DISTRIBUTION IN GaAs
USING RADIOACTIVE TRACER ^{14}C

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ABSTRACT

Microscopic segregation of carbon in GaAs has been studied using autoradiography of a crystal doped with radioactive tracer ^{14}C . The autoradiographs were compared to images of the wafers obtained by photoetching and by high resolution scanning photoluminescence microscopy. It was found that the carbon distribution is homogeneous within the limit of the resolution of the radiographs of about $15\text{ }\mu\text{m}$ and that there is no correlation between the carbon distribution and the luminescence contrast.

1. INTRODUCTION

Carbon is always present in LEC grown GaAs single crystal at a concentration level of about $5 \times 10^{15} \text{ cm}^{-3}$. In Bridgman grown materials, its concentration is usually about one order of magnitude lower. The presence of carbon at relatively high concentration levels has been demonstrated to be due to the presence of numerous graphite parts (mainly heaters and heat shields) in the crystal growth chamber [1]. The role of carbon as a major electrically active impurity is not yet fully understood. Carbon, a light element, is difficult to detect at these concentration levels with conventional techniques such as secondary ion mass spectroscopy. Mapping of the carbon distribution with high spatial resolution of a few microns is especially difficult. As a Group IV element, carbon has amphoteric character and can at least in principle occupy Ga or As sites. Heavily carbon-doped GaAs epitaxial films are p-type which indicates that carbon resides preferentially on As sites (C_{As}). C_{As} forms a shallow acceptor at $E_v + 24 \text{ meV}$ while C_{Ga} is not yet well-characterized but should form a shallow donor. Some results suggest that C_{Ga} is also involved in the formation of a deep center [2]. The most sensitive techniques for determining the carbon concentration are based on indirect measurements that require accurate calibration and rely on the physical rather than chemical phenomena related to the presence of carbon. In particular, local vibrational modes of carbon acceptors (neutral and negatively charged) can be detected using infrared transmission. Carbon acceptors cause three strong photo-luminescence emission lines at 1.5127, 1.493 and 1.490 eV, at 4.2 K which can be used for carbon detection.

In this paper, we report on the first direct imaging of carbon in GaAs using radioactive tracer ^{14}C . In addition, the wafers were characterized using Hall measurements, photoetching and scanning photoluminescence microscopy.

2. EXPERIMENTAL

One GaAs: ^{14}C crystal was grown in a horizontal Bridgman configuration using our multi-zone computer-controlled furnace [3]. In the Bridgman-type furnace, the radioactive GaAs compound is confined in a vacuum-sealed quartz ampoule which prevents its release to the ambient and contamination of the crystal puller. $\text{Ba}^{14}\text{CO}_3$ was chosen as the source of ^{14}C because of its availability in a convenient crystalline form. $\text{Ba}^{14}\text{CO}_3$ is added to the gallium prior to synthesis. During synthesis of the 800 grams GaAs charge by vapor transport reaction in the growth ampoule, decomposition of $\text{Ba}^{14}\text{CO}_3$ at high temperature releases the ^{14}C to the melt. The growth run was initiated directly following synthesis of the radioactive compound without cooling and reloading of the ampoule. The growth rate was 4mm/hour, the axial temperature gradient over the solid measured on top of the ampoule was $10^\circ\text{C}/\text{cm}$, the melt temperature was 1242°C and the As source temperature was 617°C . $\text{Ba}^{14}\text{CO}_3$ was enriched at 59 millicuries per millimole ^{14}C . An amount of about 82.5 mg with a total activity of 25 millicuries was used to provide an average ^{14}C concentration of $10^{17}/\text{cm}^3$ in the crystal assuming that all the ^{14}C would reside in the GaAs.

The presence of Ba is a major handicap for growth of a single crystal since steep temperature gradients are required to prevent constitutional supercooling and polycrystallinity. The axial temperature gradient of $10^\circ\text{C}/\text{cm}$ was not sufficient to prevent interface breakdown at a very short

distance from the seed. This problem was also encountered by Brozel et al. [4] who used BaCO_3 as a source for ^{13}C . However, we subsequently considered the polycrystallinity as an advantage since it allowed us to image any segregation of carbon at grain boundaries as well as in the single crystal domains.

After growth the crystal was cut in wafers both perpendicular and parallel to the growth direction. The wafers were subsequently lapped and polished using Al_2O_3 slurry and a Syton/ H_2O_2 / H_2O solution, respectively.

The polished wafers were then placed on a film sensitive to β radiation (Kodak XAR, double-coated) for auto-radiography. The resolution of the radiographs is limited by grain size of the film emulsion. A slightly higher resolution can be achieved by maintaining the film at very low temperatures (-80°C) during the period of exposure. The resolution on our radiographs is about 15 to 20 μm . A blank sample (undoped GaAs) was placed on the film together with the doped wafers as a reference to make sure that the blackening of the film was not due to artifacts such as mechanical damage of the emulsion or others.

3. RESULTS

The actual presence of carbon in the ^{14}C -doped crystal was inferred from Hall measurements taken along the crystal. The measurements were compared to results obtained with an undoped GaAs crystal grown under identical conditions (Fig. 1). The main impurity present in these crystals is silicon, a donor, introduced in the melt by the reduction of the silica boat. It is not possible from Hall measurements to determine the total carbon concentration in the GaAs: ^{14}C crystal, due to the

ill-defined amphoteric behavior of both silicon and carbon and due to the lack of information on other residual impurities. However, the lower net-donor concentration measured in the ^{14}C -doped crystal indicates an increase in the number of compensating acceptors of the order of a few times 10^{16}cm^{-3} , most likely due in part to C_{As} and in part to other impurities. Ba, a group II impurity, should form an acceptor on Ga sites, however, no information is available in the literature on this impurity. Surface activity measurements performed on polished wafers indicate a ^{14}C concentration of the order of $5 \times 10^{15}\text{cm}^{-3}$. Both the Hall effect and surface activity measurements indicate that only a fraction of the ^{14}C was incorporated in the GaAs. A major fraction of the ^{14}C remained at the interface between the crystal and the crucible. This is corroborated by the strong beta activity leading to strong film exposure along the periphery of the wafer.

Figures 2 and 3 show autoradiographs of ^{14}C -doped wafers cut perpendicular and parallel to the growth direction, respectively. The autoradiographs show that ^{14}C was incorporated in the crystal from seed to tail and that within our resolution limit ^{14}C distribution is homogeneous in a wafer. There is no evidence of precipitates and preferential segregation at grain boundaries. The autoradiographs reveal the presence of grains of different orientation nucleated at the bottom of the crucible. It suggests that the segregation coefficient for carbon varies with orientation. Such effects have been observed in Si [5,6] and Ge [7]. On radiograph 2(b), striations are clearly visible in the lower part of the wafer. Figure 3 also shows that the carbon concentration increases from seed to tail. It is an indication that the segregation coefficient of carbon in GaAs is less than unity. However, quantitative

determination of ^{14}C is needed to clarify this point since we have no precise proof that complete mixing of ^{14}C in the melt was achieved prior to growth.

Direct comparison of the autoradiographs with microphotographs obtained after photoetching and with images obtained from high resolution scanning photoluminescence are shown in Figures 4 to 6. The experimental set-up and procedures for photoetching and scanning luminescence have been described previously [8,9]. The areas on the wafer have been selected as representative of dislocated areas (Fig. 4), areas with low angle grain boundaries (Fig. 5) and areas with a grain boundary (Fig. 6). The correlation between photoetching and photoluminescence, which has been reported previously [9], is clearly visible: around dislocations an area with a higher etching rate corresponds to an area with higher luminescence intensity while a low etching rate at the dislocation core corresponds to a lower luminescence intensity. Wakefield et al. [10] attributed the high intensity luminescence to preferential segregation of shallow acceptors such as C_{As} around dislocations. On our images, the luminescence intensity is due to the sums of the intensities of several transitions because a Krypton laser was used with a photon energy larger than the GaAs bandgap. We could not detect any correlation between the photoetched or luminescence images and the autoradiographs. Preferential segregation of carbon is not detected, neither around dislocations nor at grain boundaries. Therefore, we conclude that the increase in luminescence intensity around dislocations is not due to segregation of carbon. It must be noted that the autoradiographs cannot reveal local atomic rearrangements. Precipitation of arsenic at the dislocation core can locally drive amphoteric impurities into shallow acceptor positions which,

in turn, would increase the luminescence intensity. These results appear to confirm the interpretation of Hunter [11] that a change in carrier lifetime in the "denuded" areas around dislocations rather than their concentration is responsible for the bright luminescence.

In summary, we conclude, based on our ^{14}C autoradiographs, that within the limits of our photographic emulsion resolution of about 15 μm , we cannot detect any carbon segregation near dislocations or grain boundaries and that the increase in luminescence intensity around dislocations is not due to segregation of carbon.

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FIGURE CAPTIONS

Fig. 1 Carrier concentration versus fraction solidified for undoped GaAs crystal and GaAs:¹⁴C crystal grown in a quartz crucible under identical growth conditions. Data were obtained from Hall measurements on samples cut in the center of the crystals along the growth direction.

Fig. 2 Autoradiograph of GaAs:¹⁴C wafers cut perpendicular to the growth direction:

(a) at 5.4 cm from the seed

(b) at 13.6 cm from the seed.

Fig. 3 Autoradiographs of wafers cut parallel to the growth direction in the center of the crystal.

Fig. 4 (a) GaAs:¹⁴C after photoetching

(b) scanning photoluminescence image of same area as in (a)

(c) autoradiograph of same area as in (a).

Fig. 5 (a) GaAs:¹⁴C after photoetching

(b) scanning photoluminescence image of same area as in (a)

(c) autoradiograph of same area as in (a).

Selected area includes a grain boundary and a low-angle grain boundary.

Fig. 6 (a) GaAs:¹⁴C after photoetching

(b) scanning photoluminescence image of same area as in (a)

(c) autoradiograph of same area as in (a).

Selected area includes grain boundaries.

Figure 1.

XBL 875-8887

(a)

(b)

XBB 874-3039A

1 cm

Figure 2.

XBB 875-3925A

Figure 3.

XBB 875-3924

Figure 4.

XBB 875-3922

Figure 5.

XBB 875-3923

Figure 6.

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