

B3-1 Application of radioactivation analysis for the determination
(INVITED) of trace amounts of elements in semiconductor materials

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Determination of trace amounts of elements has recently attracted special interest in semiconductor technology, because the electrophysical properties are greatly affected by the presence of trace amounts of elements and by their distribution. The determination of these elements, however, is very difficult. Although the ordinary analytical methods such as spectrophotometry, atomic absorption spectrometry and spark-source mass-spectrometry, etc, are sensitive to most elements, the practical application of these methods is limited when the impurity elements of interest at level of ppb are analysed. Radioactivation analysis is one of the most useful methods for these purposes.

In this paper, the author summarizes the principle of radioactivation analysis and the application to the study of semiconductor materials.

1. Radioactivation analysis

Radioactivation analysis is based on the formation of radioactive nuclides as a result of reactions between high-energy particles (neutron, proton, deuteron, α -particle and γ -ray, etc) and the isotopes of the elements of interest in the test sample.

The method has many excellent points compared with any ordinary analytical method:

- (1) Although the sensitivity of determination varies by the value of the activation cross-section and the condition of irradiation, the sensitivity in many elements is extremely high than the other analytical methods.
- (2) Any secondary contamination into the irradiated sample does not introduce any error for the determination.
- (3) The yield in the chemical separation can be corrected by the measurement of the carrier content.

2. γ -ray spectrometry and substoichiometric radioactivation analysis

In general, radioactivation analysis is classified into two methods. One is the non-destructive method and the other is the destructive one. In the case of the non-destructive method, the technique of γ -ray spectrometry using Li-drifted Ge-detector is mainly employed. By using the multi-channel

pulse-height analyser coupled with Ge-detector, a large number of elements can be measured simultaneously without any chemical separation.

When the matrix produces radioisotopes of comparable half-lives as the element to be determined, chemical separation becomes unavoidable. In ordinary destructive radioactivation analysis, however, a laborious and time-consuming isolation is necessary for the preparation of the sample for measurement, and the chemical yield needs to be determined.

Substoichiometric radioactivation analysis¹⁾²⁾ is advantageous for the determination of elements by the destructive method. In the substoichiometric method, it is necessary that the chemical separation is carried out with a smaller amount of reagent than that is required to react with total amount of the element in question. This method is much simpler and more rapid than the ordinary destructive radioactivation analysis and high selectivity can be expected. Furthermore, the correction for the chemical yield is not necessary.

3. Application of radioactivation analysis to the study of semiconductor materials

Radioactivation analysis is a useful method for the study of semiconductor materials and a number of papers have been published³⁾.

Determination of trace amounts of elements in gallium arsenide, high-purity metals and glass, and glassmaking materials was studied by the substoichiometric and non-destructive radioactivation analysis. The substoichiometric method has been applied for the determination of cadmium, copper, gold, indium, manganese, nickel, silver, tin and zinc, and the non-destructive γ -ray spectrometry was employed for the determination of chromium, iron and rare earth elements. Cobalt was determined by both methods. The concentration of the impurities in these materials became clear by these experiments. The content of the impurities in the gallium arsenide (a carrier concentration is $3.0 - 4.8 \times 10^{16}$ n/cm³ and a mobility is 4500 - 5100 cm²/V/sec) was given as follows; Cd 12, Cu 22 - 96, Au 0.06 - 0.07, Mn 1, Ni 21 - 31, Ag 0.09 and Zn 13 - 15 ppb⁴⁾. This result suggests that most p-type impurities in gallium arsenide are present in concentrations lower than 100 ppb.

Determination of the diffusion profile of zinc in gallium arsenide is required as a fundamental information for the preparation of diodes of gallium arsenide. The substoichiometric radioactivation analysis has been applied for the determination of diffusion profile of zinc and it has been shown that

the diffusion profile can easily be determined⁵⁾. An analogous method has been applied to the determination of the diffusion profiles of cadmium and tin⁶⁾⁷⁾.

Diffusion of gold into silicon and evaporation of arsenic from silicon were also studied by the γ -ray spectrometry using NaI detector⁸⁾⁹⁾.

On the other hand, the contamination of copper introduced during the preparation processes of gallium arsenide wafers and the effect of chemical etching in the determination of indium in metallic zinc were studied by the substoichiometric method¹⁰⁾¹¹⁾. It was found that the contamination of copper was mostly governed by the quality of quartz used for the heat treatment and the content of indium was varied by the etching depth.

Some other interesting examples will be introduced.

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