# 2. Semiconductor Research with Reactor Neutrons

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## ABSTRACT

Reactor neutrons play an important role for characterization of semiconductor materials as same as other advanced materials. On the other hand reactor neutrons bring about not only malignant irradiation effects called radiation damage, but also useful effects such as neutron transmutation doping and defect formation for opto-electronics. Research works on semiconductor materials with the reactor neutrons of the Kyoto University Reactor (KUR) are briefly reviewed. In this review, a stress is laid on the present author's works.

## INTRODUCTION

Atomic and mesoscopic structures of semiconductor crystals can be analyzed by neutron diffraction (ND) and neutron small angle scattering (NSAS), respectively. For instance, A. Okazaki et al. found an abnormal crystal structure of silicon with a neutron diffractometer of KUR [1]. An oxygen precipitate process in Czochralski-grown silicon crystal was studied with a NSAS spectrometer at KUR by T. Takeda et al. [2]. Frequency distribution of phonons or phonon spectrum of semiconductor crystals can be obtained by neutron inelastic scattering (NIS), but more intense neutron beam may be desirable for NIS spectrometry than that of KUR.

Characteristics of semiconductor materials are strongly governed by very small amount of impurity elements and lattice defects. Reactor neutrons are of great use to measure some of these quantities. Because of its excellent sensitivity, neutron activation analysis (NAA) is widely applied to analyze not only impurity elements in a matrix of semiconductor materials, but also impurity distributions close to their surface. By making use of a radioactive isotope with considerably short half life as a tracer, dynamic behaviour of impurity distributions in semiconductor materials can be also observed, and these radioactive isotopes are mainly produced by reactor neutron irradiation. A few examples are shown later. Profiles of boron distribution close to a surface of semiconductor materials can be also obtained by neutron depth profiling (NDP), however none of NDP work has been attempted in KUR so far. We may apply prompt gamma-ray analysis (PGA) using neutron capture reactions to impurity analysis of semiconductor materials, but none has tried this technique at KUR yet.

When we irradiate a semiconductor material with neutrons especially with fast ones, atoms in a crystal lattice are knocked on and there arise lattice defects which are often called radiation damage. On the other hand, when a constituent nucleus in a semiconductor material captures a thermal neutron and then its residual nucleus converts to a new element by beta decay, this newly produced nucleus often acts as a new dopant in the original matrix. The most typical example is the $^{30}Si$ $(n,\gamma)$ $^{31}Si$ reaction and $^{31}Si \rightarrow {}^{31}P + \beta^- + \bar{\nu}$, by which phospher is doped in the silicon matrix. This technique is called neutron transmutation doping (NTD). The NTD for silicon has been developed and is now already in practical use. In Japan silicon of about 110 tons (estimated value in 1990) is processed by NTD and the NTD silicon is widely used for manufacturing power electronic elements. When we irradiate a semiconductor material with reactor neutrons, radiation damages take place together with NTD. These damages are often annealed by heating a specimen, but all of the behaviours about the radiation damages for semiconductor materials have not been elucidated yet. Using KUR, a large number of research works on radiation damage of semiconductor materials have been carried out so far. The present author is now trying to compare the radiation damage of silicon caused by the KUR neutrons with those by other reactor and accelerator neutrons. A part of newly obtained data is shown later.

## IMPURITY ANALYSIS

Trace elements in an intrinsic semiconductor material can be analyzed by NAA, one of which is instrumental neutron activation analysis (INAA) and the other radiochemical NAA (RNAA). T. Takeuchi et al. obtained many impurity elements in silicon with KUR by INAA [3]. Their detection limit and an example of their results are cited in Figs. 1 and 2, respectively.

More than 20 years ago staff from Osaka University and the present author jointly started to study spatial distribution of impurity elements close to their surface. For example [4], the distributions of antimony atoms which were ion-implanted into silicon wafers at elevated temperatures is shown in Fig. 3. From this data, we found an enhanced diffusion effect of the antimony atoms in silicon.

K. Yokota et al. of Kansai University joined this group later and we tried to develop a technique of radioactive ion implantation. A radioactive isotope such as $^{76}As$ and $^{115}Cd$ was produced at a hydraulic conveyor of KUR and was loaded in an ion source of a small accelerator, with which these radioactive ions were accelerated about 45kV and were implanted into semiconductor wafers [5]. In order to investigate stability of a compound semiconductor namely GaAs during thermal processes, $^{76}As$ ions were implanted into GaAs wafers. The surface of the GaAs wafers was covered by $SiO_2$ or by $Si_3N_4$. Finally, we found that the surface GaAs layer covered by $SiO_2$ decomposed but that covered by $Si_3N_4$ didn't as shown in Fig. 4 [6]. A large number of similar works have been carried out by this group so far.

I. Ohdomari et al. of Waseda University and the present author attempted to study redistribution of implanted arsenic atoms in silicon wafers during metallic silicide formation [7]. After arsenic atoms were implanted into a silicon wafer, paradium was vacuum-evaporated on it and this wafer was heated at 250℃ to form a $PdSi_2$ layer. During this paradium silicide formation, the redistribution profiles of arsenic atoms were observed by INAA using KUR. As shown in Fig. 5, we found an extraordinary rise at the front boundary of silicon and named this "snowplow effect" of impurity atoms in silicon during silicide formation. However we also found that there is no snowplow effect in the case of molybdenum silicide formation [8].

## IRRADIATION EFFECTS

Research on radiation damage of semiconductor materials has a long history and a huge number of works on this subject have been carried out using reactor neutrons together with other various radiations. This subject is decribed and discussed in many textbooks and review papers, but it is pointed out that further more study is still required to elucidate radiation damage model from its primary process to its final stage. A more quantitative evaluation of radiation damage of semiconductor materials by reactor neutrons should be investigated, in which the approach to use so-called damage function may be recommendable.

At KUR several groups have irradiated semiconductor materials not only in common irradiation facilities such as pneumatic tubes but also in a low temperature irradiation loop (LTL). Very recently N. Fukuoka et al. of Naruto University of Education irradiated a germanium crystal at the temperature of 25K in LTL of KUR and found two levels below its conduction band [9]. They also studied the nature of oxygen donors and radiation defects in oxygen-doped silicon recently [10]. In this work, the neutron irradiation was made in the pneumatic tube of KUR.

K. Kuriyama et al. of Hosei University and the present author began NTD study of compound semiconductors, mainly GaAs, several years ago. When GaAs is irradiated by reactor neutrons, germanium ($^{70}$Ge and $^{72}$Ge) and selenium ($^{76}$Se) atoms are produced from gallium atoms ($^{69}$Ga and $^{71}$Ga) and arsenic atoms ($^{75}$As), respectively, and both germanium and arsenic atoms are expected to act as donors in the GaAs matrix. However these NTD atoms are usually not in the original positions but are displaced into interstitial ones. In addition, the defects induced by fast neutron irradiation disturb the electrical activation of NTD impurities. We irradiated GaAs wafers in three different positions of KUR, namely an in-core plug (P-1), a hydraulic conveyor (P-2) and a graphite thermal column (P-3). Figure 6 shows the electric resistivity as a function of annealing temperature [11]. There is a remarkable difference in the recovery process between the samples irradiated at P-1 (or P-2) and P-3. The abrupt change or decrease in electric resistivity of P-1 or P-2 around 400℃ is assumed to be based on the hopping conduction. The increase in that around 500℃ is associated with the disappearance of the hopping conduction. This assumption of the hopping conduction was proven by photoconductance measurements. Recently M. Satoh and K. Kuriyama have actively performed more works related to the NTD GaAs crystals [12]. Two coworkers of this group, T. Kawakubo and M. Okada of Research Reactor Institute, Kyoto University tried to measure electron spin resonance (ESR) spectra and Fourier transformed infrared (FTIR) absorption spectra of both GaAs and GaP after irradiation of reactor neutrons [13]. Their results together with other earlier data are comprehensively reviewed in a recently published paper by T. Kawakubo[14].

Y. Nishida et al. of Osaka University irradiated several types of diamonds with the neutrons of KUR and observed color centers by means of optical and ESR measurements [15]. They are aiming at searching for the possibility of opto-electronics applications of the color centers in these diamonds. Although diamond is not a semiconductor but an insulating material, the objectives of this work is so interesting and creative that I introduce it here.

Very recently we started to study irradiation effects of silicon by reactor neutrons with several different spectra, 14MeV neutrons from the D-T reaction with a low energy accelerator and charged particles with medium energy accelerators. Results are compared with each other and with the calculated ones. The electrical resistivities of four type silicon wafers with different oxygen contents were measured after the neutron irradiations at the Glory Hole in the Fast Source Reactor of the University of Tokyo, YAYOI and at three positions in KUR. An example of these measurements is shown in Fig. 7 [16]. It can be seen that the electrical resistivity of all silicon wafers increases with fast neutron fluence. This increment of the electrical resistivity is due to the trap of carriers by some defects which are created by the neutron irradiation. We are going to measure deep level defects with a deep level transient spectrometer (DLTS) and to observe lattice disorders by Rutherford backscattering (RBS) very soon.

## CONCLUSION

Making use of the neutrons of KUR, a large number of research works about semiconductor materials have been carried out by many groups for about 27 years. Their results have markedly contributed the progress in semiconductor science and technology. A research reactor has been and will be really a powerful and useful tool not only to characterize semiconductor materials, but also to reform significantly their characteristics. More semiconductor research with research reactors is expected and to be enhanced in future.

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* : The present author is one of the coauthors of these papers.

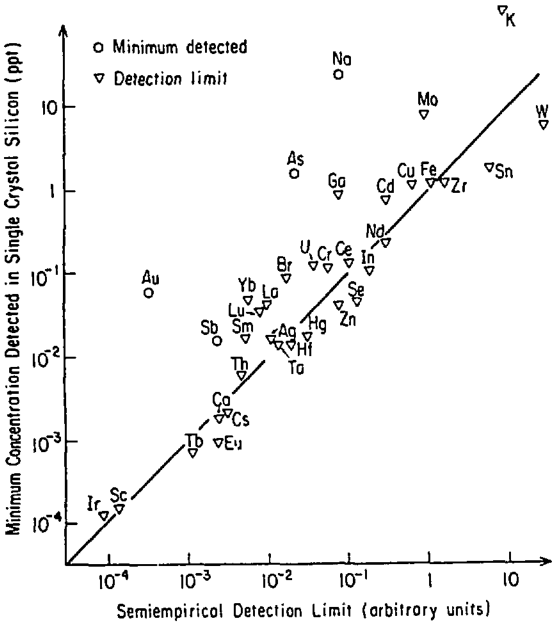

Fig. 1 Minimum concentration detected in a silicon crystal versus a semiempirical detection limit
(T. Takeuchi et al. [3])

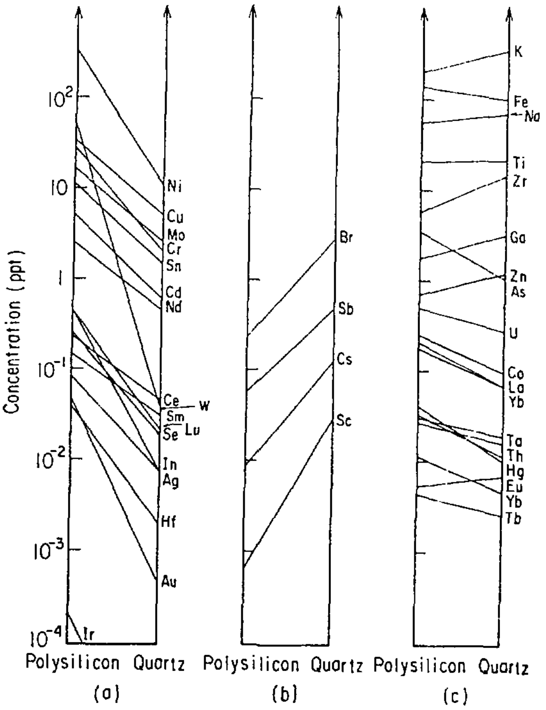

Fig. 2 Comparison of impurity consentrations in polysilicon and quartz ($\times 10^{-3}$) measured by INAA (T. Takeuchi et al. [3])

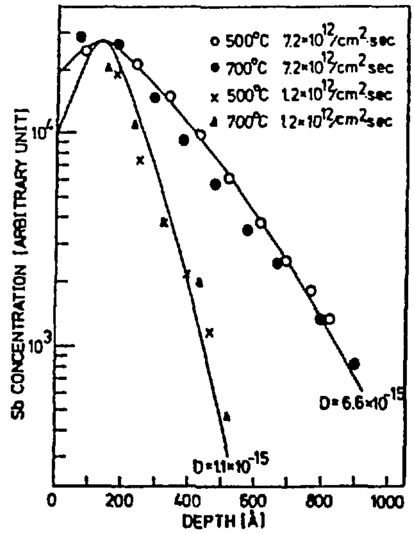

Fig. 3 Spatial distributions of ion-implanted antimony atoms in silicon measured by INAA (K. Gamo et al. [4])

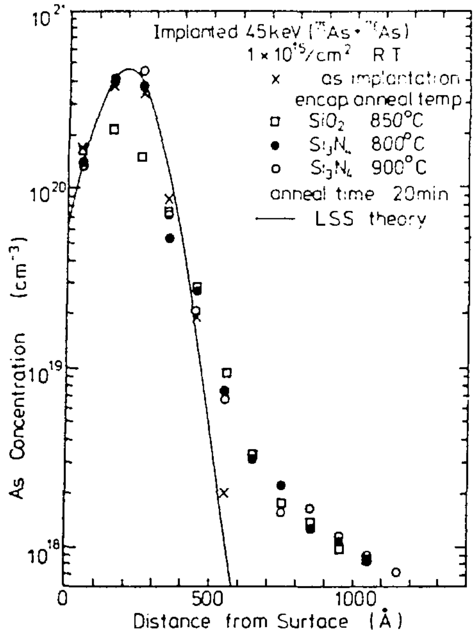

Fig. 4 Spatial distributions of radioactive-ion-implanted arsenic atoms in GaAs encapulated by $SiO_2$ and $Si_3N_4$ (K. Yokota et al. [6])

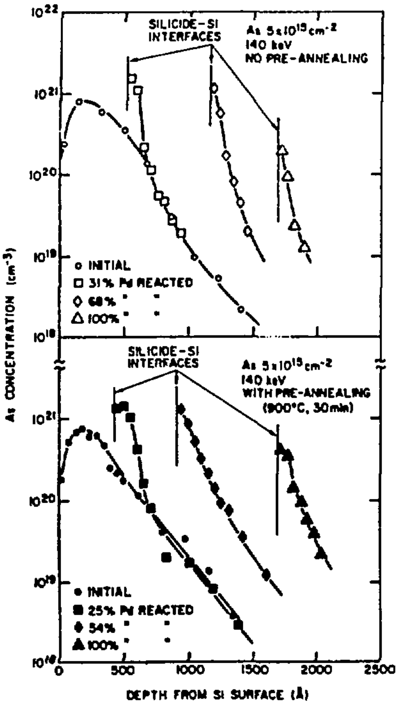

Fig. 5 Variation of spatial distributions of ion-implanted arsenic atoms in silicon during $Pd_2Si$ formation measured by INAA (I. Ohdomari et al. [7])

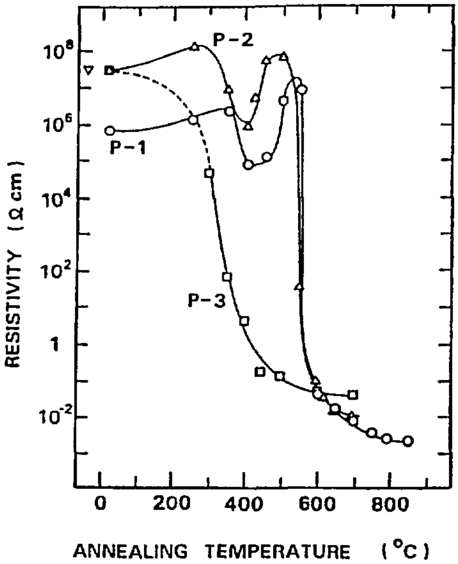

Fig. 6 Electrical resistivity of reactor neutron irradiated GaAs versus annealing temperature. P-1, P-2 and P-3 show the positions in KUR and are described in text. (M. Satoh et al. [11])

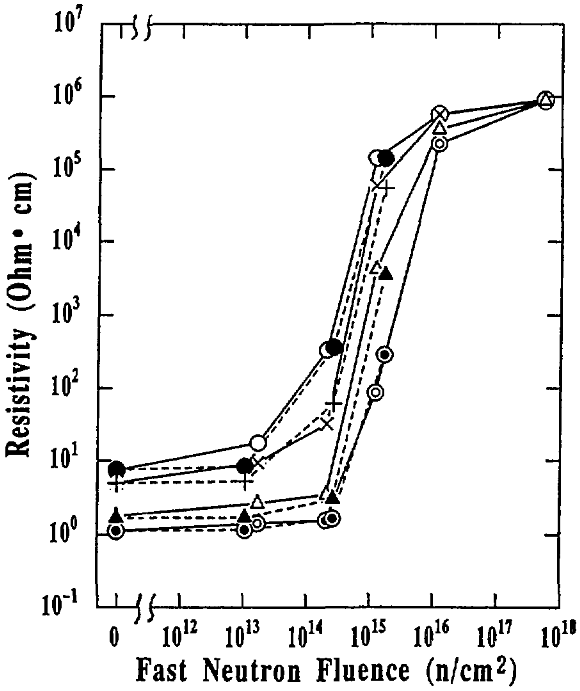

Fig. 7 Electrical resistivity of four type silicon wafers with different oxygen contents versus fast neutron fluence [16].