Determination of uranium in powdered quartz at ppb level by fission track method

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Uranbestimmung in Quarzpulver im ppb-Bereich mit Hilfe der Kernspurmethode

Zusammenfassung. Da im Bereich der Halbleiterindustrie eine steigende Nachfrage nach Quarzpulver mit niedriger Alpha-Aktivität besteht, wurde die Uranbestimmung in hochreinem Quarzpulver mit Hilfe einer vereinfachten Kernspurmethode untersucht, bei der jeweils etwa 0,5 g der Probe und des Kernspurdetektors (synthetisches Quarzglasplättchen mit etwa 0,04 ppb U) in eine Polyethylenkapsel gegeben und mit einem thermischen Neutronenfluß von etwa 10^{17} cm^{-2} bestrahlt wurden. Ein einfaches Verfahren zum chemischen Ätzen der Spuren wurde angewendet. Alle Messungen der Urankonzentration wurden relativ durchgeführt durch Vergleich der unbekannten Spurdichten mit denen von Standardglas NBS SRM 617. Die Zuverlässigkeit des Verfahrens wurde bis herab zu etwa 0,1 ppb U geprüft. Die in den untersuchten Proben gefundenen Urankonzentrationen lagen im Bereich von 7,9 bis 0,12 ppb.

Summary. The demand for powdered quartz with low alpha -radioactivity has been increasing in the field of manufacturing semiconductor memory device packages. In this work, the determination of uranium in powdered high-purity quartz samples was studied using a simplified fission track procedure in which ~0.5 g each of sample and a fission track detector (synthetic quartz glass plate, uranium impurity ~0.04 ppb) were loaded in a polyethylene capsule and irradiated with a thermal neutron flux of ~10^{17} cm^{-2}. An easy procedure was also employed for chemical etching of fission tracks. All measurements of uranium concentration in the samples were made on a relative basis by comparing the unknown track densities to that measured for NBS glass SRM 617. The reliability was established for the present determination of uranium down to ~0.1 ppb. The concentrations of uranium in powdered quartz samples studied in this work were in a range from 7.9 down to 0.12 ppb.

Introduction

The passage of ionizing radiation through semiconductor memories has been shown to change the logical state of individual memory cells [5]. Since the problem, what is known as soft error of computer, originates mainly from alpha-rays emitted from the surface of the memory device package, not only packaging materials with low alpha-radioactivity, but also accurate analytical techniques for trace alpha-ray emitters such as uranium have strongly been desired in the field of electronics related to semiconductor memory devices. At the present state in development of denser semiconductor memory devices, an alpha-ray emission rate of less than 10^{-3} cm^{-2} h^{-1} is desired. An acquisition time in the order of months is necessary for a reliable measurement of alpha-ray emission rates at this level by means of currently used alpha counting methods which have a large effective area, e.g. ~100 cm^{-2}. On the other hand, such a desired extent of alpha-ray emission rates from the surface of memory device packages roughly corresponds to uranium concentrations lower than 2 ppb, in the case where ^{238}U and ^{232}Th are contained in the packages uniformly, the activity ratio of $^{232}Th/^{238}U$ is unity, and radioactive equilibria in uranium and thorium decay chains are achieved.

The fission track method is a non-destructive procedure which can be highly selective and sensitive for natural uranium by appropriate selection of the fission track detector and neutron irradiation conditions [3]. By this method, the determination of uranium from 7.5 ppm down to 1.5 ppb in materials related to semiconductor memory devices was achieved by Riley [6], who showed that the fission track method is capable of determining natural uranium concentrations below 0.04 ppb by using high-purity fused silicia as a fission track detector and by irradiating specimens with a thermal neutron flux of ~10^{19} cm^{-2}, while uranium at ppb levels could be determined with poor reliability by typical non-destructive neutron activation analysis [4].

Powdered high-purity quartz is one of the materials with potential low alpha-radioactivity, and is, therefore, in demand as a raw material to manufacture semiconductor memory device packages. Furthermore, a simplified and reliable technique is desired for routine analysis of uranium at ppb levels in powdered quartz.

In the present work, the determination of traces (0.1 ~10 ppb) of uranium in powdered high-purity quartz has been studied by the fission track method. In order to facilitate the application of the fission track method in the routine determination of uranium at ppb levels in powdered samples, procedures for preparing neutron irradiation specimens and for chemical etching of fission tracks have been simplified.

Experimental

Samples and reference materials

Powdered high-purity quartz samples, supplied for the present work (Table 2), are commercially available materials for

filler material of semiconductor memory device packages: two samples among seven were powdered rock crystals (natural quartz crystal); three among seven were powdered fused quartz glasses manufactured from rock crystal; the rest were powdered synthetic quartz glasses. Individual powdered samples were sieved to obtain a grain size fraction <0.15 mm.

The primary standard material used in the present uranium determination was glass standard reference material (SRM) 617 (72.37 ± 0.89 ppb U; $^{235}U/^{238}U$ atomic ratio $= 0.00616 \pm 0.00001$ [2]; nominal composition: 72% SiO_2, 14% Na_2O, 12% CaO, 2% Al_2O_3), which is available from the National Bureau of Standards (NBS). Rock reference material (RM) JB-2 (powdered basalt; grain size <0.15 mm; uranium concentration by preliminary analysis at GSJ: 170 ~ 210 ppb), which is available from the Geological Survey of Japan (GSJ), was used as a secondary reference material.

Fission track detector

A high-purity synthetic quartz glass plate, Viosil-SMS, which is available from Shin-Etsu Quartz Products Co., Ltd., Japan, was employed as the fission track detector for this work. The Viosil-SMS, inherently manufactured as a synthetic quartz substrate for hard surface integrated circuit photomask, was chosen for the following reasons: (1) the lowest uranium concentration (~0.04 ppb) among commercially available fission track registration media which were examined preliminarily by the fission track method; (2) extremely low density of surface defects which will disturb fission track counting; and (3) hard surface resistive against abrasion by powdered quartz. The Viosil-SMS quartz glass plate (75 mm × 75 mm × 1.5 mm), of which the two faces were protected with adhesive tape in advance, was cut into small pieces (10 mm × 5 mm, 1.5 mm thick) by using a diamond wheel cutter. The pieces — fission track detectors — thus obtained were removed from adhesive tape, numbered serially by using a diamond glass cutter, washed with acetone, 2 M HNO_3, distilled water, and methanol, successively, and dried. The final washing with methanol and subsequent drying were carried out in a Teflon bottle.

Procedures

In the conventional fission track procedure, the powdered sample is generally put tightly in a small hole (e.g., 3 ~ 5 mm in diameter) drilled in an appropriate holder (e.g. polycarbonate). In the present work, handling of powdered samples to prepare neutron irradiation specimens was carried out in a simple and easy way as described below.

The powdered quartz sample, unless otherwise specified further (Table 2), was washed in a Teflon bottle with 1 M HNO_3, distilled water, and methanol, successively. A piece of washed fission track detector was placed in a polyethylene capsule (6 mm i.d., 17 mm internal height) lengthwise, and powdered quartz, dried after the washings, was then loaded. The amount of powdered quartz loaded in a capsule was from 0.4 to 0.5 g. Prior to use, the polyethylene capsule was washed in a Teflon bottle with 2 M HNO_3, and distilled water, successively, and dried. Each specimen, prepared in the way mentioned above, was plugged and sealed in a polyethylene bag.

Table 1. Response of NBS glass SRM 617 to fission track counting

Neutron irradiation time (h)	Relative thermal neutron flux[a]	Net fission track density[b] (cm^{-2})	Normalized[c] net fission track density (cm^{-2})
50	61.92 ± 1.24	40820 ± 910	659 ± 20
5	6.63 ± 0.23	4386 ± 96	662 ± 27
1	1.288 ± 0.051	829 ± 35	644 ± 37
0.5	0.656 ± 0.029	449 ± 26	684 ± 50
0.1	0.1300 ± 0.0068	78 ± 12	600 ± 101
			mean: 650
			mean σ: 31

[a] 61.92 relative thermal neutron flux corresponds approximately to 1.26×10^{17} cm^{-2} actual thermal neutron flux

[b] Corrected for blank fission track density [(26 ± 3) cm^{-2}/(61.92 relative thermal neutron flux)]

[c] Fission track density normalized to 1 ppb natural uranium concentration and to 61.92 relative thermal neutron flux

On the other hand, in order to evaluate the blank concentration of uranium in the fission track detector itself, four pieces of fission track detectors at a time were put in layers and vacuum sealed in a polyethylene bag.

Pieces (~5 mm × ~5 mm, 1 mm thick) of the NBS glass SRM 617 were soaked in 0.5 M HNO_3 for 1 min, in distilled water for 0.5 min, and in methanol for 0.5 min, successively, and dried in a Teflon bottle. Each piece of the NBS glass SRM 617 thus cleaned was sandwiched between two fission track detectors and vacuum sealed in a polyethylene bag. The GSJ rock RM JB-2 was loaded into a polyethylene capsule together with a fission track detector in the same way as mentioned for powdered quartz.

Except for the washing procedures, all the sample handling mentioned above was performed in a large polyethylene bag, one bag for each sample, so as to minimize external and cross contaminations. Prior to the following neutron irradiation, in order to monitor the thermal neutron flux, stainless steel wire (0.5 mm in diameter) weighing ~30 mg was winded around each sealed specimen in a polyethylene bag. The specimens with neutron flux monitors were then placed in an irradiation tube (31 mm i.d., 65 mm internal height) which has a capacity for 21 specimens.

Neutron irradiations were carried out in the TRIGA-II nuclear reactor at Musashi Institute of Technology, Japan, at a thermal neutron flux rate of $\sim 7 \times 10^{11}$ cm^{-2} s^{-1}. The duration of neutron irradiation was 50 h (i.e., 5 h/day × 10 days) for the determination of uranium in powdered quartz, and was from 6 min to 50 h for an examination of response of the NBS glass SRM 617 to the present fission track counting. Since the irradiation tube was placed in the cooling water of the reactor, annealing of fission tracks by heating was avoided.

After neutron irradiation and subsequent cooling for about one week, the fission track detectors were taken out of the irradiation specimens, rinsed briefly in distilled water to remove sample powder, and dried. Radioactivities in the fission track detector after the cooling of about a week was negligibly low. Then, the fission track detector, placed one by one in a polyethylene test tube with a ~4 mm ϕ hole in the bottom, was immersed in 46% HF at ~20°C for 2 min to etch fission tracks on the surface of the fission track detector. Ultrasonic vibrations were applied to the etching

Table 2. Natural uranium concentrations of powdered high-purity quartz samples

Sample	U (ppb)
Rock crystal	
RC-1 (quarried in China, 3rd class[a])	0.31 ± 0.04
	0.32 ± 0.04
	0.35 ± 0.04
	0.37 ± 0.05
RC-2 (quarried in Brazil, 1st class[a])	0.18 ± 0.03
	0.20 ± 0.03
	0.21 ± 0.04
	0.25 ± 0.04
Fused quartz glass (manufactured from rock crystal)	
FQ-1 (from washed[b] RC-2)	0.36 ± 0.04
	0.39 ± 0.05
	0.41 ± 0.05
	0.44 ± 0.05
FQ-2 (from unwashed RC-2)	1.8 ± 0.1
	1.8 ± 0.1
	1.9 ± 0.1
	2.0 ± 0.1
FQ-2 (from unwashed RC-2, unwashed prior to present analysis)	2.2 ± 0.1
	2.4 ± 0.1
	2.4 ± 0.1
	2.5 ± 0.1
FQ-3 (origin unknown, commercially available)	7.7 ± 0.2
	7.9 ± 0.2
	8.0 ± 0.2
	8.0 ± 0.2
Synthetic fused quartz glass	
SQ-1 (commercially available)	0.09 ± 0.03
	0.11 ± 0.03
	0.12 ± 0.03
	0.14 ± 0.03
SQ-2 (commercially available)	2.0 ± 0.1
	2.2 ± 0.1
	2.2 ± 0.1
	2.2 ± 0.1

[a] Classified according to transparency
[b] With 2M HNO_3 at room temperature for 1 h

solution (46% HF) in a Teflon bottle. At the end of each etching period, the fission track detector in the holed test tube was transferred into two successive distilled water baths placed in an ultrasonic cleaner, then taken out of the test tube to flush with a stream of distilled water. The present etching procedure is simple and easy in handling small fission track detectors.

For each stainless steel neutron flux monitor, gamma -ray spectrometry was carried out by the use of a Ge(Li) gamma-ray spectrometer. From the relative concentration of ^{60}Co induced in each flux monitor, the relative thermal neutron flux on each specimen was evaluated.

All measurements of fission track density were carried out by the use of a TV-monitor connected to an optical microscope. One counting area of 250 μm × 200 μm on the surface of the etched fission track detector, illuminated with transmitted light, was magnified to a picture of 225 mm × 180 mm on the TV-monitor. Under the present experimental conditions, the fission tracks were readily visible and distinguishable from any other surface imperfections, and tracks with diameters ranging from 5 to 10 μm were counted with the naked eye. By scanning two faces of each fission track detector, fission tracks in ~ 0.8 cm^2 at the widest were counted for each sample. Since the fission track densities were low, the time required for counting tracks in one field of view was ~ 3 s. In the case where the fission track density exceeded 2×10^3 cm^{-2}, fission track counting was carried out using random fields of view, and $\sim 10^3$ tracks were counted for each sample. Fission track countings for blank fission track detectors were carried out using the faces contacted with neighbouring detectors.

By corrections for blank and relative thermal neutron flux, net fission track densities were obtained, and uranium concentrations in individual samples were calculated from the net fission track densities. The calculation was carried out on a relative basis where fission track densities measured for the NBS glass SRM 617 and for the GSJ rock RM JB-2 were references. In the calculation of uranium concentration, 61.92 ppb was assumed in the primary standard, the NBS glass SRM 617, as the effective concentration of uranium with natural isotopic composition, since the $^{235}U/^{238}U$ atomic ratio in the SRM 617 is 85.6% of common natural uranium [2]; while natural isotopic composition was assumed for uranium in JB-2 and powdered quartz samples.

Results and discussion

The first analytical problem which arose in the present work was presented by the blank fission tracks resulted from uranium impurities in the fission track detector itself. By measurements of fission track densities in 12 blank fission track detectors, it was justified to assume that the blank density is essentially constant for the detectors used in this work, if the tracks were counted over a area of more than 0.35 cm^2 per sample. From the densities measured, the average concentration of uranium in the blank fission track detector was determined to be (0.040 ± 0.005) ppb.

The second analytical problem was the reliability of fission track counting at low track density. Since the lowest uranium concentration among the NBS glass SRMs with certified uranium concentration and isotopic composition is 72.37 ppb in the SRM 617, the range of linearity of the measurable fission track density relative to uranium concentration down to 0.1 ppb must be examined. For this purpose, the response of the NBS glass SRM 617 to the fission track counting procedure was studied by irradiating a specimen, consisting of the SRM and the fission track detector, with varying thermal neutron fluxes. In this approach, prior to placing into contact with the SRM 617, the fission track detectors were irradiated for 50 h in the TRIGA-II nuclear reactor with a thermal neutron flux rate of $\sim 7 \times 10^{11}$ cm^{-2} s^{-1}. This pre-irradiation of the fission track detector for 50 h and subsequent irradiation for a short time (e.g. 0.1 h) with the SRM 617 approximately realized an irradiation situation in which the fission track detector is irradiated for 50 h with a sample containing uranium at low concentrations. Table 1 contains the results of this response examination. The accompanying errors in this table are $\pm 1\sigma$ errors due to counting statistics. The response of the NBS glass SRM 617 to the present fission track counting was given in terms of normalized net fission track density, and the results shown in Table 1 indicate that the response is quite linear and reproducible over a range of thermal neutron flux shown in this table. This suggests that the present fission track

counting is reliable in a range of density which corresponds to a natural uranium concentration down to 0.1 ppb, if specimens were irradiated for 50 h or longer at a thermal neutron flux rate of $\sim 7 \times 10^{11}$ cm^{-2} s^{-1}.

In the present work (quartz samples being supplied in powdered form, while the primary standard in plate form), clearances between fission track detector and material studied by the fission track procedure were different between powdered sample and plate formed standard. Although the difference was anticipated as a source of error, it was obviated by the relatively long ranges of fission fragments in air (16 ~ 29 mm [1]). Furthermore, since the chemical composition of quartz is close to that of glass SRM, potential differences in neutron self-shielding and significant differences in fission fragment ranges were considered to be minimized. On the other hand, the GSJ rock RM JB-2 differs in chemical composition from that of quartz and NBS glass SRM. Hence, in the case where JB-2 is referred to as a comparator, the apparent value of uranium concentration (i.e. without any corrections for difference in matrix), which was evaluated referring to the NBS glass SRM 617, was employed for the calculation of the uranium concentration in powdered quartz. The apparent concentration of uranium in JB-2 was evaluated to be (174 ± 5) ppb.

The analytical results of uranium in powdered quartz are given in Table 2 together with $\pm 1\sigma$ errors due to counting statistics. The reproducibility of repeated determinations was verified within $\pm 2\sigma$ error. This implies that contamination of the samples with uranium during preparation of neutron irradiation specimens could be minimized to a level not exceeding the 2σ error of uranium concentration given in Table 2.

For FQ-3 (which showed the highest uranium concentration among the samples studied in this work by the fission track method) other analytical methods for uranium were attempted; i.e., non-destructive neutron activation analysis and radiochemical method using alpha-ray spectrometry. For the neutron activation and radiochemical analyses standard solution of uranium prepared from the NBS SRM 960 was employed as a reference. By non-destructive neutron activation analysis (1 g of FQ-3 was irradiated for 5 h in the TRIGA-II nuclear reactor at a thermal neutron flux rate of $\sim 7 \times 10^{11}$ cm^{-2} s^{-1} and gamma-ray spectrometry of ^{239}Np was carried out) a result showing (8 ± 2) ppb of uranium was obtained. By the radiochemical method (30 g of FQ-3 were decomposed, the calibrated ^{232}U tracer was added, and alpha-ray spectrometry was carried out after chemical separation of uranium and electrodeposition) a result showing (8.4 ± 0.7) ppb of uranium was obtained. The agreement was excellent among the analytical results of uranium in FQ-3 studied by the fission track method, non-destructive neutron activation analysis and radiochemical analysis.

The comparison of results for RC-2, FQ-1 and FQ-2 shows that appropriate washing of powdered quartz is suitable before using it for manufacturing semiconductor memory device packages with a uranium concentration as low as possible. In unwashed FQ-2, clusters of uranium were detected by the fission track method, and this fact suggests that the sample has received some surface contamination with uranium before forwarding to the market.

Acknowledgement. The author wishes to thank the members at the Atomic Energy Research Laboratory, Musashi Institute of Technology, for their invaluable assistance in the neutron irradiations.

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Received August 2, 1986