Available online at www.sciencedirect.com

ScienceDirect

Journal of Nuclear Materials 357 (2006) 31–47

journal of nuclear materials

www.elsevier.com/locate/jnucmat

The effect of annealing at 1500 °C on migration and release of ion implanted silver in CVD silicon carbide

H.J. MacLean [a], R.G. Ballinger [b,*], L.E. Kolaya [c], S.A. Simonson [c], N. Lewis [c], M.E. Hanson [c]

[a] *Idaho National Laboratory, Idaho Falls, Idaho, USA*
[b] *Massachusetts Institute of Technology, Department of Nuclear Science and Engineering, 77 Massachusetts Avenue, Bldg NW-22-117, Cambridge, MA 02139, USA*
[c] *Lockheed Martin Corporation, Schenectady, New York, USA*

Received 20 October 2004; accepted 8 May 2006

Abstract

The transport of silver in CVD β-SiC has been studied using ion implantation. Silver ions were implanted in β-SiC using the ATLAS accelerator facility at the Argonne National Laboratory. Ion beams with energies of 93 and 161 MeV were used to achieve deposition with peak concentrations of approximately 26 wt% at depths of approximately 9 and 13 μm, respectively. As-implanted samples were then annealed at 1500 °C for 210 or 480 h. XPS, SEM, TEM, STEM, and optical methods were used to analyze the material before and after annealing. Silver concentration profiles were determined using XPS before and after annealing. STEM and SEM equipped with quantitative chemical analysis capability were used to more fully characterize the location and morphology of the silver before and after annealing. The results show that, within the uncertainty of measurement techniques, there is no silver migration, via either inter- or intra-granular paths, for the times and temperature studied. Additionally, the silver was observed to phase separate within the SiC after annealing. The results of this work do not support the long held assumption that silver release from CVD SiC, used for gas-reactor coated particle fuel, is dominated by grain boundary diffusion.

PACS: 61.72.Yx; 61.80.−x; 66.30.−h; 66.30.Jt

1. Introduction

The standard TRISO-coated particle fuel design used for high temperature gas reactor fuel consists of a fuel kernel surrounded by successive layers of: (1) low-density pyrocarbon, (2) high-density pyrocarbon, (3) silicon carbide (SiC) and (4) high-density pyrocarbon. The SiC layer serves as the main barrier to fission product release. Although most fission products, such as cesium, iodine, xenon, and krypton, are retained by the combination of pyrocarbon and SiC layers, previous observations of silver release during fuel testing and operation raises concerns that the SiC layer may not be as effective for

* Corresponding author. Tel.: +1 617 253 5118; fax: +1 617 253 0807.
E-mail address: hvymet@mit.edu (R.G. Ballinger).

0022-3115/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2006.05.043

silver. Silver release from SiC coated fuel increases the total activity levels in the primary circuits of high-temperature gas reactors which makes maintenance more difficult and costly.

Silver release has been observed from reportedly or reputed to be intact fuel, suggesting that silver is transported through intact silicon carbide layers. In many cases, experimental measurements of silver release was observed to exhibit a temperature dependence that has been interpreted as a sign of a diffusive mechanism. In most cases, however, silver release has been reported for either a batch of fuel particles or an entire fuel element, leaving uncertainties about individual particle performance. In cases where fission product release from individual particles has been measured, and where individual coated particle characteristics and radiation environments have been essentially identical, silver release, as characterized by rates, timing, and release fractions, has been highly variable. In some cases the release fraction has varied from 0% to 100% among nominally identical particles. This type of behavior is not consistent with a thermally activated process where classical Arrhenius temperature dependence would be expected for all particles.

In previous work, Nabielek et al. implanted low energy silver ions into SiC disk samples at room temperature and measured the concentration profiles before and after annealing [1]. They observed no change in the silver concentration profile after exposure for 30 min at 1180 °C and reported a 'maximum' value for the diffusion coefficient of approximately $1 \times 10^{-19}\,m^2/s$ based on assuming that the actual migration was just below the minimum sensitivity of their detection method. Nabielek et al. attributed their results to silver ions becoming trapped in silicon carbide grains during implantation and not being able to diffuse along grain boundaries.

Although the results of Nabielek et al. were inconclusive, their annealing experiment was conducted at a very low temperature, 1180 °C, with respect to the SiC melting point of 2830 °C and for a very short time. Assuming that a vacancy transport mechanism would be operative one would not expect significant matrix diffusion below approximately half of the absolute melting temperature. Grain boundary diffusion would be of the order 1000× faster than matrix diffusion, but even if this were the transport mechanism the rate would be very slow. For these reasons Nabielek would not be expected to have observed diffusion if a vacancy mechanism were operative. Although there are no directly measured diffusion data for silver reported in the literature in SiC, there are data for other atoms of similar size. Data from Bernhok et al. for aluminum and gallium in 6H–SiC indicate diffusion coefficients in the range 10^{-18}–$5 \times 10^{-16}\,m^2/s$ in the temperature range 1800–2300 °C [2]. Extrapolation of these data to lower temperatures yields values of approximately $10^{-15}\,cm^2/s$ and $10^{-20}\,m^2/s$ at 1500 °C and 1100 °C, respectively. In contrast, reported values of diffusion coefficients, assumed to be grain boundary transport, from silver release measurements have been of the order $10^{-17}\,m^2/s$ and $5 \times 10^{-13}\,m^2/s$ at 1000 °C and 1800 °C, respectively. Thus, there appears to be a significant discrepancy between observed release-based derived diffusion coefficients and what might be expected based on comparison, albeit only approximate, with other similar size atoms, even if grain boundary diffusion is assumed.

Because of the potential significance that a more detailed understanding of the migration of silver in SiC could have for the design of advanced coated particle fuel systems, a program has been under way for the past three years to develop this understanding. Initial results of this program have been reported elsewhere [3,4]. As a part of this program, experimental measurement of the diffusion coefficient of silver in SiC has been a primary goal. Ion implantation experiments have been conducted to investigate silver behavior in SiC at 1500 °C. This temperature was chosen based on the reported literature values for migration of silver in SiC. At this temperature the rates were anticipated to be rapid enough to be easily measured with adequate accuracy. Additionally, this temperature corresponds to the upper operating temperature range for advanced high temperature gas reactor coated particle fuel. These systems make use of SiC as a primary barrier to fission product release. Silver is one of the elements of significant concern for these systems. This paper reports on the results of this program.

2. Experimental

2.1. Materials

Flat plate, CVD SiC, 0.3 cm thick, was the starting material for the ion implantation experiments. The material was obtained from Coorstek, Inc. The reported density was $3.21\,g/cm^3$ with grain sizes in the range of 3–10 μm, preferentially oriented in