

Inert gases as a probe for chemical, physical or structural changes in solids

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Abstract

Using measurements of diffusion and the release of inert gases from solids as a probe for observing and understanding chemical, physical or structural changes in solids is a mature technique which has gained significantly from the more than 25 years of dedicated work by Professor Balek. Useful relationships for predicting the behaviour of new systems can often be established in this way. As an example, some data on the behaviour of rare gases in the semiconductors Si, Ge, GaAs and SiC are reported here. Other examples include the oxidation of some metals, the recrystallization of cold-worked silver and the in-service behaviour of advanced nuclear fuels.

INTRODUCTION

Inert gases are largely insoluble in crystalline solids but do nevertheless occur in some solids, e.g. in natural uranium ores, where both helium and the heaviest rare gas, emanation (Em) or radon (Rn), are formed in situ as decay products in the natural decay chain of uranium. Inert gases can also be willingly introduced into some solids by means of a number of techniques, including doping with a precursor such as radium, or by controlled ion implantation with energetic, often mass separated, ions. When measuring the gas release, data and information can be obtained on a number of processes, including the diffusional release of gas, the interaction of the gas with lattice defects, the precipitation of the gas into gas-filled bubbles, and the chemical and structural changes that occur in the investigated solid, since changes in the defect state and, in particular, phase changes often cause an abrupt release (burst) of rare gas. The rare-gas behaviour can thus be used as a convenient probe for such solid-state changes. Professor Balek has devoted more than 25 years to applying and perfecting the particular method of observing the behaviour of emanation with regard to the thermal

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behaviour of solids. He has recently summarized and described the potential of this method in a monograph entitled "Emanation Analysis and other Radiometric Emanation Methods" [1].

There is an impressive tradition of work on (radioactive) rare gases. This is convincingly proven by the work of three famous Nobel Laureates: Mme M. Curie [2] who first reported emanation to exist; Lord Rutherford [3] who first observed the temperature dependence of the emanating power; and Otto Hahn [4] who with his coworkers, established the emanation method as a probe for detecting phase changes and for investigating the surface changes of solids.

The present author joined the field in 1958, by adding recoil doping of ^{222}Rn into oxides by adsorbing ^{226}Ra on their surfaces as a means of introducing the rare-gas probe into the solid [5]. This interest immediately caused the author to become acquainted with related work by V. Balek (see, for example, ref. 6), even before either of us had received our Ph.D. degrees.

Much of the subsequent work of Professor Balek and myself remained in the general field of exploiting the unique possibilities of rare gases as solid-state probes, although the methods applied changed: to emanation thermal analysis and ion implantation. In the following, some examples of the use of rare gases as probes for solid-state processes in semiconductors, metals and ceramic nuclear fuels are given, where the rare gases were introduced into solids by means of ion implantation in an electromagnetic mass separator with simultaneous acceleration of the ions.

EXPERIMENTAL

Ion implantation is a very powerful technique for introducing otherwise insoluble rare gases into solids. By varying the ion energy, the depth beneath the surface of the solid can be varied to a large extent (from a few nanometres to many micrometres) and the concentration can be varied from trace amounts to a few atom%. Ion implantation was the technique used to detect radiation-induced phase changes and amorphization (the formation of metamict, aperiodic structures) in previously crystalline solids [7,8]. A typical penetration curve of accelerated xenon ions for well-annealed copper or silver is shown in Fig. 1.

This type of controlled ion implantation was used to label the semiconductors Si, Ge, GaAs and SiC (α -SiC of the 6H type) with radioactive rare gases (^{85}Kr , ^{125}Xe , ^{133}Xe and ^{131}Xe) to doses ranging from 8×10^{10} to 2×10^{16} ion cm^{-2} . Rutherford back-scattering (RBS) in combination with the channeling technique was used to make quantitative measurements of radiation damage and of the formation of amorphous phases. During subsequent isochronal annealing, gas release was measured as a function of temperature, and damage recovery (i.e. recrystallization of amorphous phases) was again detected by RBS/channeling.

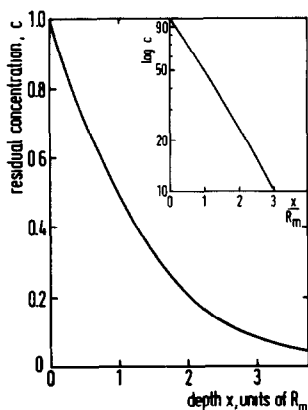


Fig. 1. Typical linear penetration curves for energetic xenon ions in copper or silver. The corresponding logarithmic plots are shown in the insert

In a similar way, cold-worked and well-annealed or single crystalline silver and foils of α -brass, copper, nickel and stainless steel were implanted with radioactive xenon ions. Following implantation, isochronal anneals were made under different atmospheres (including oxidating conditions) to obtain information on the recrystallization of the cold-worked state, or on the growth of oxide layers by using rare-gas release as a solid-state probe.

RESULTS

Semiconductors

Controlled ion implantation with mass separated heavy ions (here 0.5 MeV for ^{85}Kr and 40 keV for ^{125}Xe , ^{133}Xe or ^{131}Xe), as frequently used to produce tailor-made properties in semiconductors, also introduces radiation damage. For the four semiconductors studied here (Si, Ge, GaAs and SiC) amorphization occurred at high ion doses. The doses necessary for amorphization varied significantly for the four materials: e.g. ca. 10^{14} ions cm^{-2} for SiC and ca. 10^{15} ions cm^{-2} for Si. Figure 2(a) shows the general behaviour, the data being for SiC. Diffusional release occurs at low doses, whereas a steep release curve coinciding with the recrystallization of the radiation-damaged amorphous semiconductor is observed at high doses. The recrystallization temperature is well correlated with the melting point (T_m), i.e. it falls in the very narrow range $(0.63 \pm 0.02)T_m$. RBS/ channelling data (see Fig. 2(b)) demonstrate clearly the complete amorphization of the semiconductor (here again SiC). The peak at the surface (Si shoulder) in the implanted, aligned crystals reaches the random level.

Two more clear melting-point rules are observed for the temperatures of gas diffusion (50% gas release, Fig. 2(c)) and for the activation enthalpies (ΔH) of gas diffusion and recrystallization (Fig. 2(d)).

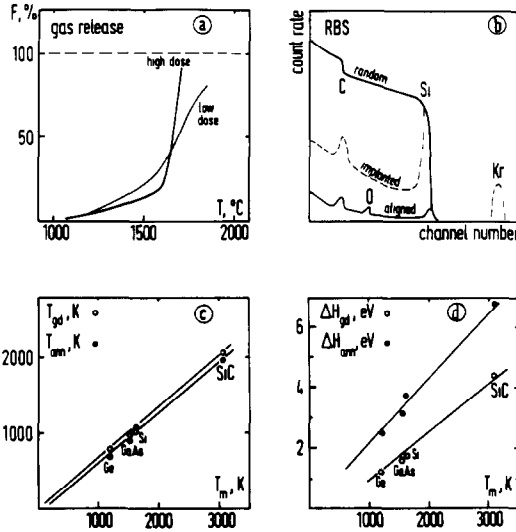


Fig 2 Rare-gas release yielding data on both gas diffusion and existence and annealing of radiation damage. The results are for the ion-implanted semiconductors Ge, Si and GaAs and, in particular, for the ceramic semiconductor 6H α -SiC. (a) Diffusional gas release of Kr from SiC at a low implantation dose compared with the release due to crystallization of the metamict surface which was amorphized on ion implantation. (b) Schematic Rutherford backscattering spectra for random direction of high dose implanted SiC and a crystal with the (0001) direction aligned with the beam. The peak labelled Si proves amorphization. (c) Temperatures for 50% gas release (T_{gd}) and for damage annealing (T_{ann}) as a function of the melting point (T_m). (d) Corresponding activation energies for gas diffusion and for damage annealing.

Metals

The range profile of implanted xenon-ions shown in Fig. 1 is typical for polycrystalline silver or copper where some channelling of the implanted ions leads to a deeper penetration. The curve with the depth expressed in units of the median or 50% range, R_m , can be approximated by the exponential equation

$$c(x) = c(0) \exp(-x/R_m) \quad (1)$$

Typical release curves for copper, α -brass, nickel and stainless steel and anneals in air are shown in Fig. 3. The release is due to oxidation because: (i) it is identical for three largely different doses — thermally activated diffusion of xenon is, in contrast, dose dependent, i.e. it is retarded at higher doses due to trapping (gas-defect interactions) or gas-bubble formation; (ii) thermally activated diffusion, as measured in inert atmospheres, occurs at significantly higher temperatures; and (iii) the fact that oxide layers grew could be demonstrated by the appearance of interference colours at the higher experimental temperatures.

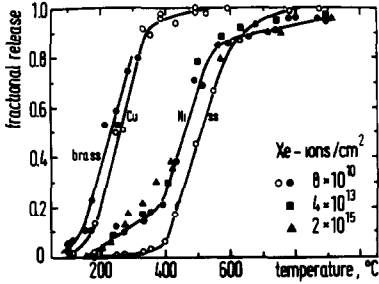


Fig 3 Gas release during oxidation of some metals α -brass, copper, nickel and stainless steel

If one assumes that the fraction of gas released corresponds to the formation of an oxide layer, the thickness of which is identical to the thickness of the metal containing the rare gas, then the fraction F of gas released can replace the fraction $c(x)/c(0)$ in eqn. (1), i.e. the thickness d of the oxide layer becomes

$$d = 2.3R_m \log F_t(T) \quad (2)$$

where the index t indicates the time of the isochronal anneal step. The results are shown in Fig. 4, with a depth scale on the right-hand ordinate for copper. The dashed line at ca. 25 Å indicates the approximate thickness of the oxide layers which grow during exposure to air at room temperature.

From eqn. (2), the rate constants k and k' can be deduced for both a parabolic law ($d^2 = kt$), or for a linear time dependence of oxidation ($d = k't$). The data shown in Fig. 4 extend the literature data to lower temperatures and yield the temperature dependence of oxidation, e.g. for copper and for 5 min anneals

$$k_{5 \text{ min}} = 10^{-9} \exp(-14000/RT) \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$$

where ΔH is in kcal mol⁻¹.

Another use of radioactive inert gases as probes for solid-state kinetics in metals is shown in Fig. 5. The isochronal release of krypton, xenon and

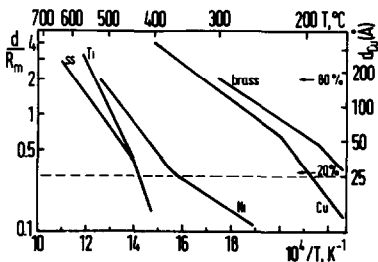


Fig. 4 Growth of oxide layers on the metals of Fig. 3 as a function of the inverse temperature. d is the thickness of the oxide layer as deduced from the release curves of Fig 3.

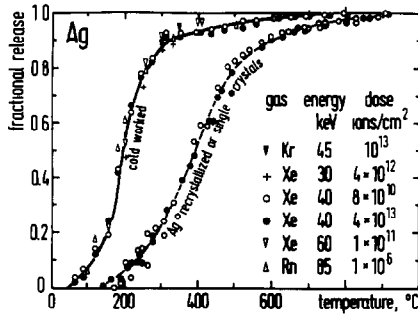


Fig 5 Release of rare gases from ion-implanted cold-worked silver and from pre-annealed polycrystalline or single-crystalline silver

radon from preannealed (recrystallized) or single crystalline silver is sigmoidal in shape, as expected for a volume diffusion process, and is described by

$$D = 0.3 \exp(-42500/RT) \text{ cm}^2 \text{ s}^{-1} \quad (3)$$

where ΔH is again in kcal mol⁻¹, the value corresponding to 1.85 eV atom⁻¹.

In contrast, release from cold-worked foils occurs at significantly lower temperatures. The release can be related to the recovery of the cold-worked state and hence to the recrystallization of the metal. Range measurements show that gas transport occurs towards the surface only, and this is attributed to sweeping by annihilating dislocations. The deduced activation

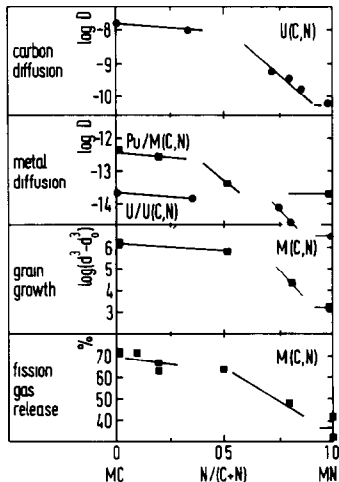


Fig 6 Typical trend of decreasing atomic mobilities in the sequence of advanced nuclear fuels carbide/carbonitrides/nitride, shown for carbon (and nitrogen) diffusion and uranium and plutonium diffusion (D at 1700 °C in cm² s⁻¹), for grain growth at 1700 °C and for fission gas release from a fast neutron irradiation at 1.2 at % burn-up (see ref 9).

enthalpy of $1.35 \text{ eV atom}^{-1}$ is in fair agreement with the literature data on the recovery of the electrical resistivity in cold worked silver.

Advanced nuclear fuels

The final example given here deals with the solid-state kinetics of advanced nuclear fuels for electricity producing fast reactors, i.e. the carbides, carbonitrides and nitrides of the actinides uranium and plutonium. These are high-melting-point ceramics with matter transport being controlled by the diffusion of the metal atoms (see the monograph on these fuels [9]). Figure 6 shows the trend of kinetics in the sequence MC/M(C,N)/MN (M = metal) for non-metal-atom (carbon and nitrogen) and metal-atom (uranium and plutonium) diffusion, grain growth and inert gas transport. In the case of a nuclear fuel, the gas is produced by fission. The gas is mainly xenon, with about 10% krypton. Once again, the gas behaviour is an indicator of solid-state kinetics.

DISCUSSION

The results presented are just a few of the many examples of how rare gases can conveniently be used as probes for investigating solid-state phenomena. Melting-point relationships are established for four semiconductors of different structure and widely different melting temperatures. This points to a diffusion and recrystallization behaviour which is more closely related to the bonding conditions than to the crystal structure. More deductions are possible, e.g. on the mechanisms involved, but this would lead us too far from the present purpose. Other examples given are low temperature oxidation of metals, where the kinetics can be followed even with very thin oxide layers, recrystallization of cold-worked silver, hence the bulk property of a metal, and finally, diffusion and high temperature kinetics in the ceramics (carbides and nitrides of uranium and plutonium) used as advanced nuclear fuels. These examples are meant to show the large potential of methods involving inert gases for investigating solid-state problems, an ever increasing field, as is clearly evidenced by, for example, the recent spectacular work on solid rare gas precipitates in ion-implanted metals which exist at or above room temperature. The field, to which Vladimír Balek devoted so much effort, is thus still young, expanding, interesting for basic science and useful for technology.

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