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## Revisiting the use of SiC as a Post Irradiation Temperature Monitor

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Silicon carbide has been used as a post-irradiation temperature monitor since first proposed for this use in 1961. The basic technique has been the repeated measurement of length of a SiC following isochronal annealing. This technique has been shown to overestimate irradiation temperature by  $\sim 100^\circ\text{C}$ . This paper discusses the use of alternate techniques, including electrical resistivity, to infer irradiation temperature. It is shown that electrical resistivity predicts irradiation temperature within  $\sim 20^\circ\text{C}$  of actual irradiation temperature. Additionally, this technique can be used in the low-temperature ( $<150^\circ\text{C}$ ) amorphization regime, and in irradiation temperatures where irradiation damage is characterized by simple defects in crystalline SiC ( $<900^\circ\text{C}$ .)

Keywords: Silicon Carbide, Temperature Monitor, Irradiation, Electrical Resistivity, Electrical Conductivity

### Introduction

Pravdyuk, et al (1961)[1] first reported that the irradiation-induced swelling of SiC begins to anneal out as the annealing temperature exceed that of the irradiation temperature. This swelling has historically been associated with lattice dilation from point defect formation as first suggested by Balarin[2], though recent modeling has suggested that small interstitial clusters[3] also may impact swelling. Swelling saturates at fluences of  $< 5 \times 10^{21} \text{ n/cm}^2$  ( $E>0.1 \text{ MeV}$ )[4,5] with an absolute change being a strong function of temperature. Figure 1 shows the saturation linear expansion that can be expected from fully dense, pyrolytic SiC.

This initial work led to widespread use of SiC as an irradiation temperature monitor. The method as described by Bramman [6] and Price[7], and later improved on by Palentine[8,9] is shown schematically in Figure 2. In this figure, the dimensions of cylindrical bars of  $\sim 1 \text{ cm}$  in length were irradiated at thermocouple measured temperatures of 525 and 772 $^\circ\text{C}$ . Post-irradiation isochronal 30 m anneals were carried out and the length of the specimens plotted. The intersection of lines (see figure 2) is

used to define the irradiation temperature. It is noted that, as swelling saturates at low fluence, and annealing occurs for temperatures above the irradiation temperature, SiC temperature monitors are giving information primarily at the end of the irradiation cycle. In the case of the data of figure 2, Price[7] quotes a temperature prediction accuracy of  $\sim 20^{\circ}\text{C}$  for the  $525^{\circ}\text{C}$  irradiation and  $\sim 30^{\circ}\text{C}$  for the  $772^{\circ}\text{C}$  irradiation through application of a 90% confidence limit. However, in Palentine's work[8], which was recently confirmed by Maruyama[10] and [11], this technique can overestimate the irradiation temperature by as much as  $100^{\circ}\text{C}$ . Palentine[9] has derived an empirical relationship between the temperature monitor intersection point and the true irradiation temperature as follows:

$$T_{\text{irr}}(^{\circ}\text{C}) = 1.0312 T_{\text{monitor}}(^{\circ}\text{C}) - 44.71 \quad ; \quad \begin{array}{cc} T_{\text{monitor}}(^{\circ}\text{C}) & T_{\text{irr}}(^{\circ}\text{C}) \\ 425 & 394 \pm 30 \\ 600 & 554 \pm 30 \end{array}$$

The  $\pm 30^{\circ}\text{C}$  in this example is due to the inaccuracy in the dimensioning of the sample. In a previous paper, Palentine[8] points out that due to the reduced swelling at the higher temperature (cf figure 1) this inaccuracy is a function of temperature:  $\pm 8$  at  $450^{\circ}\text{C}$ , and  $\pm 35$  at  $659^{\circ}\text{C}$ .

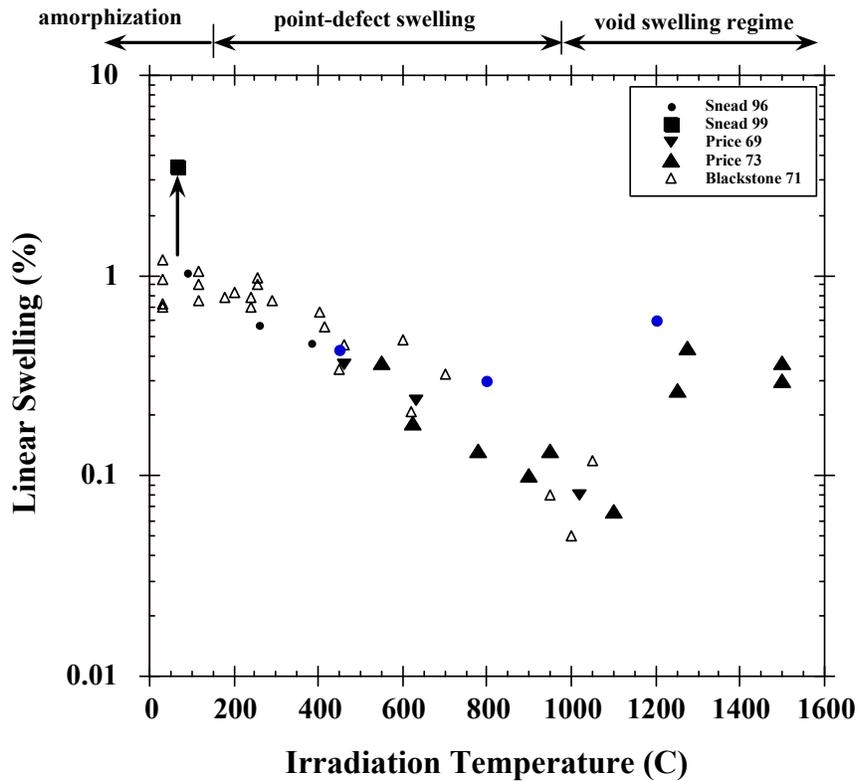


Figure 1: Saturation linear expansion of SiC as a function of irradiation temperature. Data from[5,12-15]

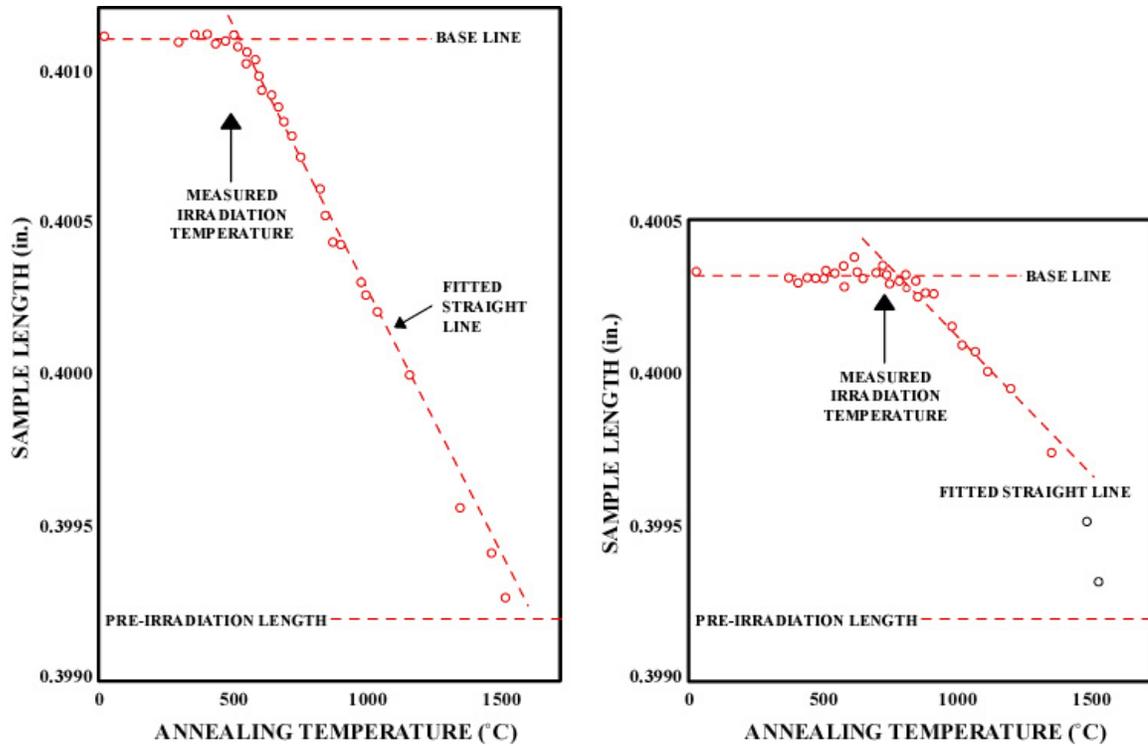


Figure 2: Application of intersection of isochronal annealing lines to determine irradiation temperature following Price[7]

In addition to using the annealing of lattice strain as the tool to measure irradiation temperature, other techniques have been presented. Specifically, Suzuki[11] and Miyazaki[16] have applied X-ray line broadening to calculate the change in lattice parameter and compare these results to the macroscopic length change. Not surprisingly, these techniques showed good agreement, though the annealing steps were relatively coarse. Price[7] and Suzuki[11] also suggests the use of electrical resistivity in combination with the similar intersection method applied to length change (ie figure 2.) Suzuki has also applied thermal expansion measurements by high-temperature X-ray diffraction.[11]

## Discussion

As discussed in the previous section, the simple application of the lines-of-intersection approach yields an overestimate of the irradiation temperature possibly due to the methodology itself, and errors intrinsic with the measurement. Therefore, one approach to improve the use of SiC temperature monitors is to tighten the accuracy of the measurement itself. For the case of dimensional measurement Palentine went to great pains to develop a system, and statistical analysis using multiple samples, to improve the accuracy of length determination to  $\pm 0.003$  mm. While this could be somewhat improved using more modern techniques, a different approach would be to use a

technique that has larger absolute changes during annealing. The following sections will briefly discuss some of the techniques recently studied. The essential point is that the accuracy of whatever technique is selected is a combination of the sensitivity and repeatability of the measurement and the change in the property that can be expected for a given annealing step. Table 1 gives such information on various techniques. This data presented is a combination of literature data (dimensioning) and routine measurement accuracies for instruments used in our laboratory.

	Measurement Accuracy	Property Change @ 500°C Irradiation	Property Recovery above irradiation temperature (%/10°C anneal)	Property change divided by measurement accuracy	Recommended Sample Type	Technique Accuracy and comments
Dimensional Change	0.0003 mm	0.5%	~ 0.007	~ 3	12.7 mm L, 3.17 mm Diam Extreme    Extreme Flatness	100°C overestimate? Measurement accuracy 12°C at T <sub>irr</sub> 450°C 70°C at T <sub>irr</sub> 700°C
Electrical Resistivity	0.01-1 %	N/A*	~ 0.3	~ 0.03	Bar 0.75 x 1 x Length	Within 20°C
Thermal Diffusivity	1 - 5%	90%	~ 0.08	~ 13	2-4 mm L, 6-10 mm diam	Within 40°C Good for when length is a limitation
Density Gradient Column	~ 0.1%	0.5%	~ 0.021%	~ 5	random, small	100°C overestimate? Within 30°C Time consuming unless multiple samples irradiated. Good for small samples
Lattice Spacing						Accuracy uncertain Time consuming

It is first important to note that a good deal of the work on SiC temperature monitors has been conducted on hot-pressed, or very low density SiC. It is well known that the presence of grain-boundary elements (such as Si or B) lead to differential swelling under irradiation. All work presented in this paper was conducted on chemically vapor deposited (CVD) SiC. This material is fully dense (3.203 g/cc) and stoichiometric.

#### *Density Gradient Column*

The density gradient column (DGC) technique, allows the direct measurement of density of solids by immersion in a column in which there is a density gradient. This technique is described by ASTM D 1505. Essentially, a heavy liquid (methylene iodide) is gradually mixed with a lighter liquid (ethylene bromide) while filling a graduated column. Over a period of as much as an hour a column is built with a gradient over the length of the column. Calibrated glass floats, which were present in the column prior to building, float along the vertical length of the column at their specific density. A plot of density-vs-

graduation is then made using these calibrated floats. A good column will be perfectly linear and when using miscible liquids will remain stable for a period of days or weeks. An example of application of the density gradient column technique is shown in Figure 3.

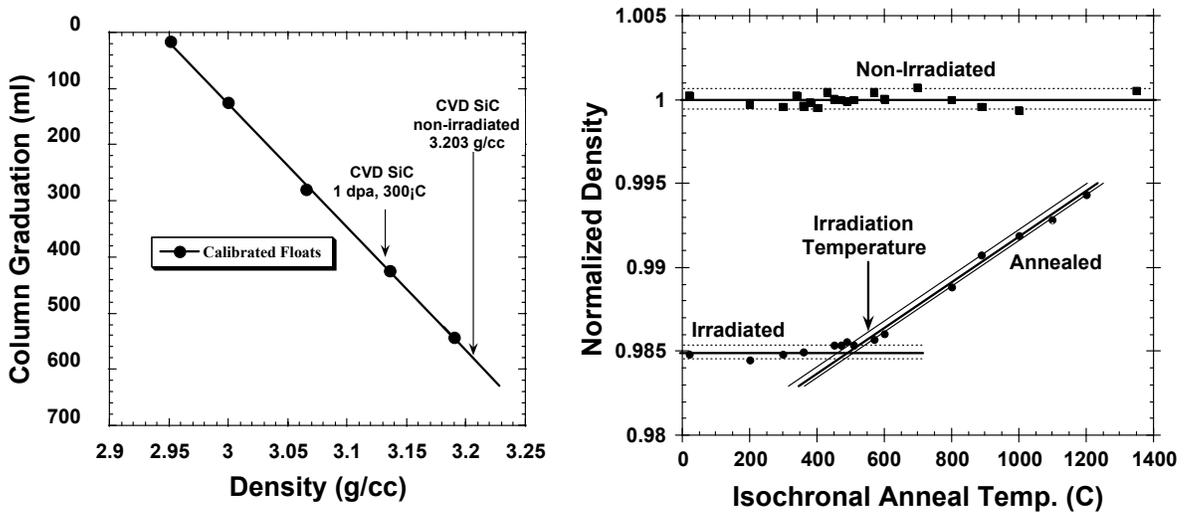


Figure 3: Application of density gradient column to temperature monitors.

The monitors in this case were fragments (<1 mm) of SiC taken from a fractured SiC disc which were individually annealed in an air furnace for a half hour and bathed in HF for 1 hr (at ambient) to remove any surface silica. Typical accuracy for a density gradient column is ~0.1%, though can be significantly improved on by decreasing the column gradient (using the entire length of the column but reducing the density range.) A typical accuracy for determining the intersection point using this technique is estimated to be  $\pm 30^{\circ}\text{C}$  by simply bounding the data and assessing the overlap as shown in Figure 3 (right.)

The advantage to the DGC technique is that it measures the change in volume fairly accurately and can be used for very small samples of arbitrary shape. If this technique is applied in a serial mode, it can be very time consuming and the cost for chemicals quite high. However, the process can be streamlined if a multiple monitors are used and annealing is carried out all at once followed by mass insertion into the DGC. If this process is followed it is important to make sure all samples are of the same initial density. As mentioned earlier, the accuracy of a temperature monitor technique depends on the relative accuracy of the measurement technique and the amount of property change that will occur during the annealing step. In comparing the DGC technique, the amount of change in density is roughly three times that of length, though without special effort, the measurement itself is less accurate. A comparison of techniques is given in Table 1 which also provides a figure of merit for comparing the various techniques. This figure of merit is simply the property change during the annealing step divided by the measurement accuracy. The larger this ratio is, potentially the more accurate the temperature monitor is. It can be seen that the length and DGC techniques are similar. For this reason, the length technique would be preferred for applications where volume is

not an issue due to its ease of application, while the DGC would be preferred for volume-limited cases.

It can be assumed that this technique, and all techniques probing swelling (eg dimension, lattice spacing, thermal expansion) will suffer from the same discrepancy between intersection point and true irradiation temperature as noted by Palentine[8] and others.

### *Thermal Diffusivity*

When temperature monitors were first suggested for use, high thermal conductivity CVD SiC was  $\sim 70$  W/m-K, while it is now commercially available from Rohm Haas with thermal conductivity of  $\sim 400$  W/m-K. Upon irradiation, the strain field associated with interstitials and vacancies act to scatter phonons and reduces thermal conductivity significantly. As with the length change, the strain in the lattice is reduced when annealed above the irradiation temperature. The measurement of thermal conductivity, or thermal diffusivity, can therefore be used as a technique for passive thermometry. Thermal diffusivity is typically measured using a thermal flash technique with either a laser or xenon flash lamp pulse illuminating a surface. The heat pulse travels through the sample and the temperature rise on the rear surface of the sample is measured with either an infrared or solid-state detector. The measured time dependent temperature rise and thickness of the sample are then used to calculate the diffusivity.

The application of this technique for temperature monitors is problematic because of the associated measurement error. Referring to table 1, a value of 1-5% inaccuracy from measurement to measurement is typical, with the infrared detector systems being less accurate than the solid-state detector systems. However, this level of inaccuracy may be reduced by more detailed attention to reduce heat loss to holder. One advantage this technique has is that it requires a relatively short sample, which is beneficial if temperature gradients are present. A second advantage is that thermal diffusivity systems are typically purchased with the ability to carry out the annealing and measurement automatically.

### *Electrical Resistivity*

Chemically vapor deposited silicon carbide is a wide band-gap semiconductor commercially available in a wide range of resistivity, from 1 to  $10^5$  ohm-cm, depending primarily on the level of doping impurities. Several competing factors contribute to the change in the as-irradiated resistivity of crystalline SiC. For example, nuclear transmutation doping will occur, increasing the donor concentration through the  $^{30}\text{Si}(n,\gamma)^{31}\text{Si}$ , and subsequent beta decay to (n-type donor)  $^{31}\text{P}$ . Additionally, 20% of the 290 wppm intrinsic (p-type acceptor) boron is removed due to the  $^{10}\text{B}(n,\alpha)^7\text{Li}$  reaction. Other impurities will also be present such as nitrogen, aluminum, etc. which also will affect the electrical resistivity. Also occurring during irradiation, the elastic collisions between high-energy neutrons and the lattice will produce simple point defects, increasing the dangling bond density, hence decreasing the material resistivity. Upon annealing of the damaged crystalline SiC, simple point defect migration will remove these dangling bonds increasing the resistivity. It is also important to note that the

electrical resistivity of SiC is a strong function of temperature. For example, a change in 1°C will change the resistivity by as much as 3.6% underscoring the need for accurate control and measurement of the testing temperature.

Figure 4 gives an example of the room temperature electrical resistivity as a function of 1.1 dpa irradiated and non-irradiated CVD SiC using the four-point probe technique. In this case a bar of 0.76 x 1 x 46 mm was used. A current of 10 mA was applied to the sample following 30 minute annealing and a room temperature bath in HF for ~ 30 minutes. The sample was seen to be ohmic by scanning from -100 to +100 mA of applied current. As given in Table 1, an inaccuracy of ~ 0.1-1% is typical for application of this technique due primarily to temperature measurement and non-uniform electrical properties along the length of the bar. Extreme care must be taken to perform the measurement on the same area of the sample to avoid these non-uniformities. Figure 4 shows a fairly large increase in the resistivity following irradiation due to the changed balance of dopants. In the absence of dopants the resistivity should have decreased from the non-irradiated value. As the temperature exceeded ~300°C the annihilation of the simple defects reduced the dangling bond density, increasing the resistivity rapidly. In contrast with the recovery in dimension or density (ie figures 2 and 3) the electrical resistivity increases in a supra-linear fashion. For this reason the intersection of lines approach used for dimensional change is not appropriate. It is suggested that the irradiation temperature using the electrical resistivity technique can be taken as the point where the resistivity begins, and consistently remains above the error band. From figure 4, the error band is the bounding of the data represented by the dotted line.

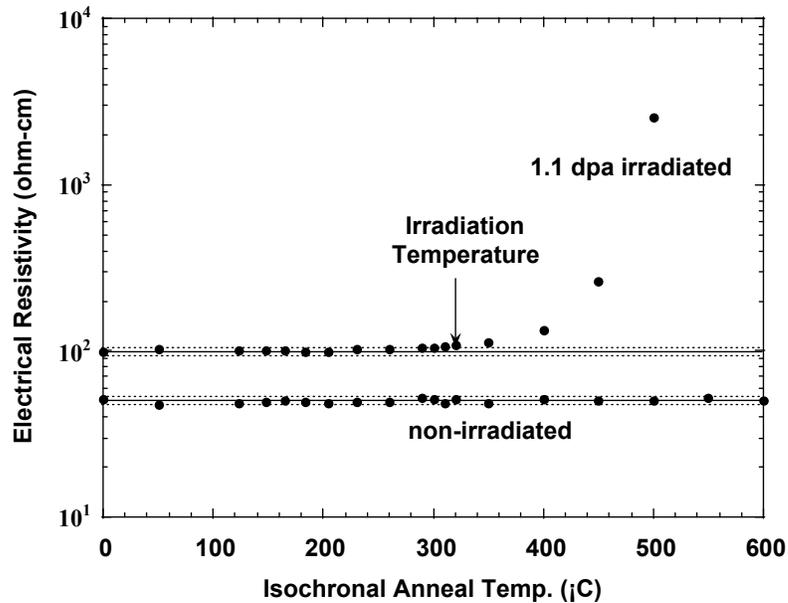


Figure 4 : Effect of annealing on the electrical resistivity of irradiated SiC.

Two important questions regarding application of this technique is whether it accurately predicts irradiation temperature and over what temperature range it can be applied. These questions are addressed with the data of figures 5 and 6. Figure 5 gives a comparison of a sample irradiated in the 14J experiment in the HFIR. The sample was Rohm Haas CVD SiC irradiated in a thermocouple-monitored capsule. The thermocouple was embedded in a graphite holder in which the CVD SiC was placed. The difference in temperature between thermocouple and samples was calculated to be  $\sim 20^\circ\text{C}$ . It is clearly seen from inspection of this curve that the point at which the resistivity begins to increase is at  $\sim 500^\circ\text{C}$ , which agrees well with the thermocouple measurement plus  $20^\circ\text{C}$ . From this it can be concluded that the electrical resistivity technique, at least at  $500^\circ\text{C}$ , is an accurate indicator of the irradiation temperature, and does not suffer from the overestimate discussed by Panentine[8] and others.

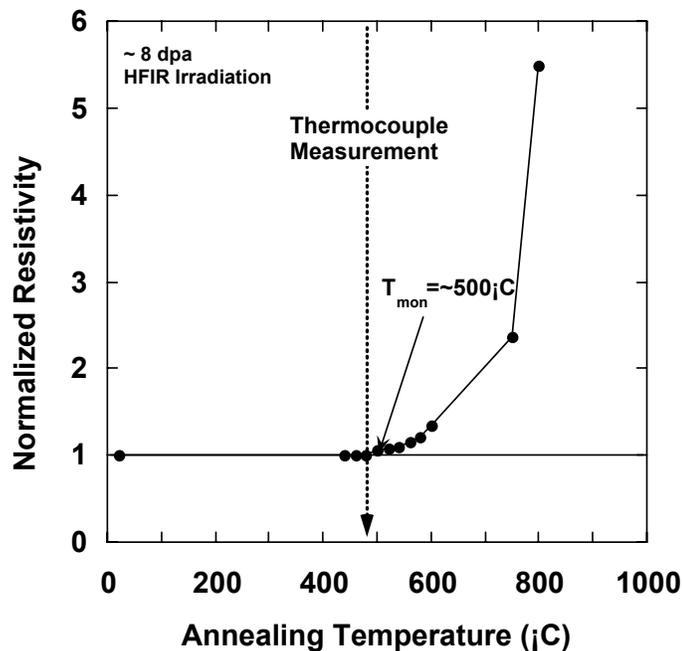


Figure 5: Comparison of in-situ measurement and post-irradiation SiC temperature monitor as measured by thermocouple and electrical resistivity technique, respectively

Figure 6 shows a series of samples, all irradiated in the HFIR core at similar dose rates of  $\sim 8 \times 10^{18} \text{ n/m}^2\text{-s}$  ( $E > 0.1 \text{ MeV}$ .) The total dose for the curves is not identical. The curve which shows an irradiation temperature of  $\sim 350^\circ\text{C}$  is at the lowest dose ( $\sim 0.1 \text{ dpa}$ , assuming  $1 \text{ dpa} = 1 \times 10^{25} \text{ n/m}^2 E > 0.1 \text{ MeV}$ ), while the remainder are from  $\sim 1\text{-}8 \text{ dpa}$ . It is speculated that the apparent saturation in normalized resistivity for the  $0.1 \text{ dpa}$  sample represents the point at which the simplest of the defects in the irradiated SiC have annealed away and represents conductivity at the new dopant level for the irradiated SiC. However, this requires further study. From figure 6 it appears that the electrical resistivity technique has a wide application temperature.

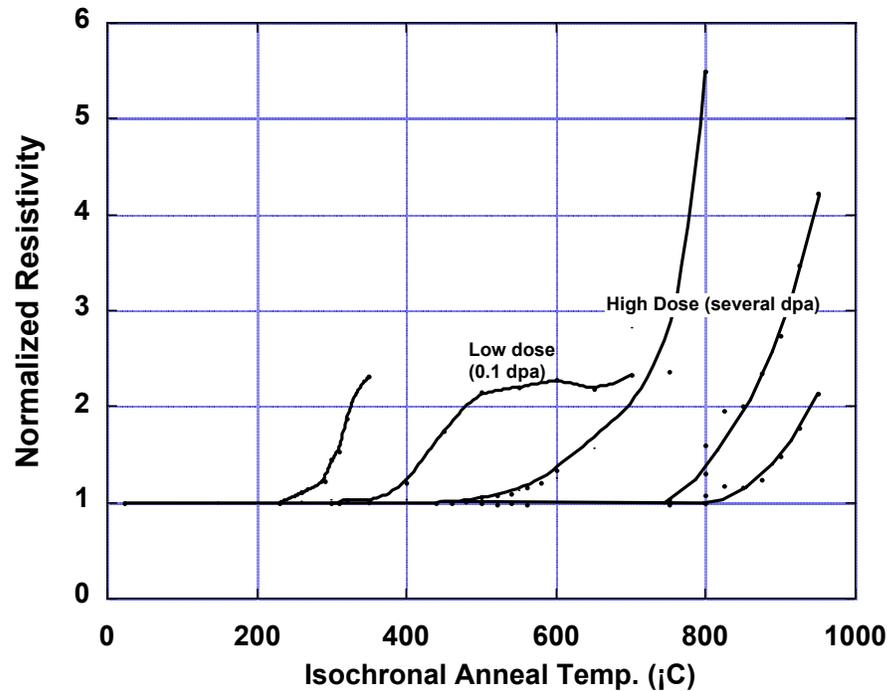


Figure 6 : Electrical resistivity technique applied over a range of irradiation temperatures.

From Table 1, the application of electrical resistivity is quoted with an accuracy of  $<20^{\circ}\text{C}$ . This has been determined based on experience and the data of figure 5. Of the techniques discussed, resistivity should be the most accurate, based on the figure of merit, because of the good measurement accuracy and the comparatively large property change in the initial annealing steps. It is likely that this technique could be more precise by extreme care in the positioning of the sample and by reducing the width of the annealing steps.

### Concluding Remarks

The use of SiC as a post-irradiation temperature monitor has been reviewed and the application of a few techniques presented. It has been shown that the techniques using dimensional change, density and electrical resistivity indicate irradiation temperature. Thermal conductivity may also be applied. However, the issue regarding the overestimation of irradiation temperature when applying the intersection-of-lines technique remains a question. It is speculated that applying any technique probing lattice strain will suffer from this problem. However, it is not clear what the basis for this overestimation is. The work of Palentine[8], which was recently confirmed by Maruyama,[10] both used impure, hot-pressed SiC. It is known that the irradiation-

induced dimensional changes in hot-pressed SiC causes non-isotropic swelling of grain boundary and matrix constituents.[17] This may alter the measurement. Further work to compare thermocouple-measured samples with dimensional change for CVD SiC would resolve this question. Furthermore, it is recommended that CVD SiC or single crystal SiC be used for all temperature monitor applications.

The use of electrical resistivity as the technique for temperature monitors appears to be a very accurate, rapid method for determining irradiation temperature over a range of temperature from ~ 200 to ~ 800°C and dose ranges from ~ 0.1 to 8 dpa. It is likely that both the upper and lower temperature ranges can be extended. Recent work by Snead and Zinkle [18] indicate that SiC which has been fully amorphized following 70°C irradiation shows as-annealed changes in density, electrical resistivity and thermal conductivity while remaining in the amorphous state. As the amorphous threshold for SiC is ~ 150°C[19] and SiC does not recrystallize before ~ 875°C [20], SiC which has been driven amorphous by neutron irradiation should work as an adequate temperature monitor in the low-temperature regime.

The upper application temperature for SiC as a temperature monitor is unclear. Referring to Figure 6, it is seen that the increase in resistivity for SiC is still sizeable above 800°C inferring that the technique can likely be applied to even higher temperatures. Further work to determine the upper application temperature is called for.

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