

# Vacancy formation energy in silicon studied by quenching under hydrogen atmosphere

M. Suezawa<sup>1</sup>, N. Fukata<sup>1,2</sup>, I. Yonenaga<sup>1</sup> and J. Vanhellemont<sup>1,3</sup>

<sup>1</sup>Institute for Materials Research (IMR), Tohoku University, Sendai 980-8577, Japan

<sup>2</sup>National Institute for Materials Science, Tsukuba 305-0047, Japan

<sup>3</sup>on leave from Department of Solid State Sciences, Ghent University, B-9000 Ghent, Belgium



## Introduction

The vacancy formation energy in Floating zone (FZ)- and Czochralski (Cz)-grown Si crystals was determined by using a thermal quenching technique during which samples are saturated with hydrogen at the quenching temperature (1). The technique is based on measuring the optical absorption due to hydrogen atoms bound to vacancies in order to estimate the vacancy concentration. In high purity FZ Si, a vacancy formation energy of 3.85 to 4.0 eV was obtained, in excellent agreement with recent estimates by Bracht and Chroneos based on self- and metal diffusion experiments and ab initio calculations (2). At high quenching temperatures, the apparent vacancy formation energy in Cz-Si seems to be lower than in FZ-Si. The reasons for this difference are discussed and elucidated.

## Experimental

Specimens were fabricated from a Cz-Si crystal with an oxygen concentration of  $5.7 \times 10^{17} \text{ cm}^{-3}$  as determined from the optical absorption coefficient at  $9 \mu\text{m}$  assuming a calibration factor of  $3.14 \times 10^{17} \text{ cm}^{-2}$ . Specimens were cut with a diamond cutting machine, mechanically shaped with SiC powder and chemically etched with a mixture of  $\text{HNO}_3$  and  $\text{HF}$  (5:1). The final specimen size was about  $6 \times 6 \times 11 \text{ mm}^3$ . Specimens were sealed in quartz capsules together with hydrogen gas. The hydrogen gas pressure was adjusted to be about 1 atm at the quenching temperature. After heating for 1 h at the quenching temperature, the quartz capsules were dropped into water. Some specimens were annealed at  $450^\circ\text{C}$  for 1 h to transform the quenched-in vacancies into  $\text{VH}_4$ , while others were isochronally annealed for 30 min at a range of temperatures with a  $50^\circ\text{C}$  interval. Optical absorption spectra were measured at about 7 K using a Fourier transform infrared (FTIR) spectrometer with a resolution of  $0.25 \text{ cm}^{-1}$ .

## Observations and discussion

As illustrated in Figs. 1, 2 and 3, in Cz-Si an additional absorption peak is observed at around  $2120 \text{ cm}^{-1}$  different from the well-known  $2223 \text{ cm}^{-1}$  peak that is associated with  $\text{VH}_4$  (3). The defects responsible for the  $2120 \text{ cm}^{-1}$  peak are proposed to be  $\text{VOH}_4$  and  $\text{VO}_2\text{H}_4$ , whereby the VO and  $\text{VO}_2$  concentrations are assumed to be determined according to the Voronkov and Falster model for grown-in defect formation in Cz-Si (4).

The formation energy of the  $2120 \text{ cm}^{-1}$  related defect as estimated from the quenching temperature dependence of the integrated intensity of the absorption peak is about 2.3 eV. The small apparent formation energy of the vacancy in Cz Si at high quenching temperatures compared to that measured in high-purity FZ, is most probably due to the interaction between vacancies and oxygen atoms. It is assumed that oxygen atoms act as a source of vacancies which allows to explain the experimental observations (3).

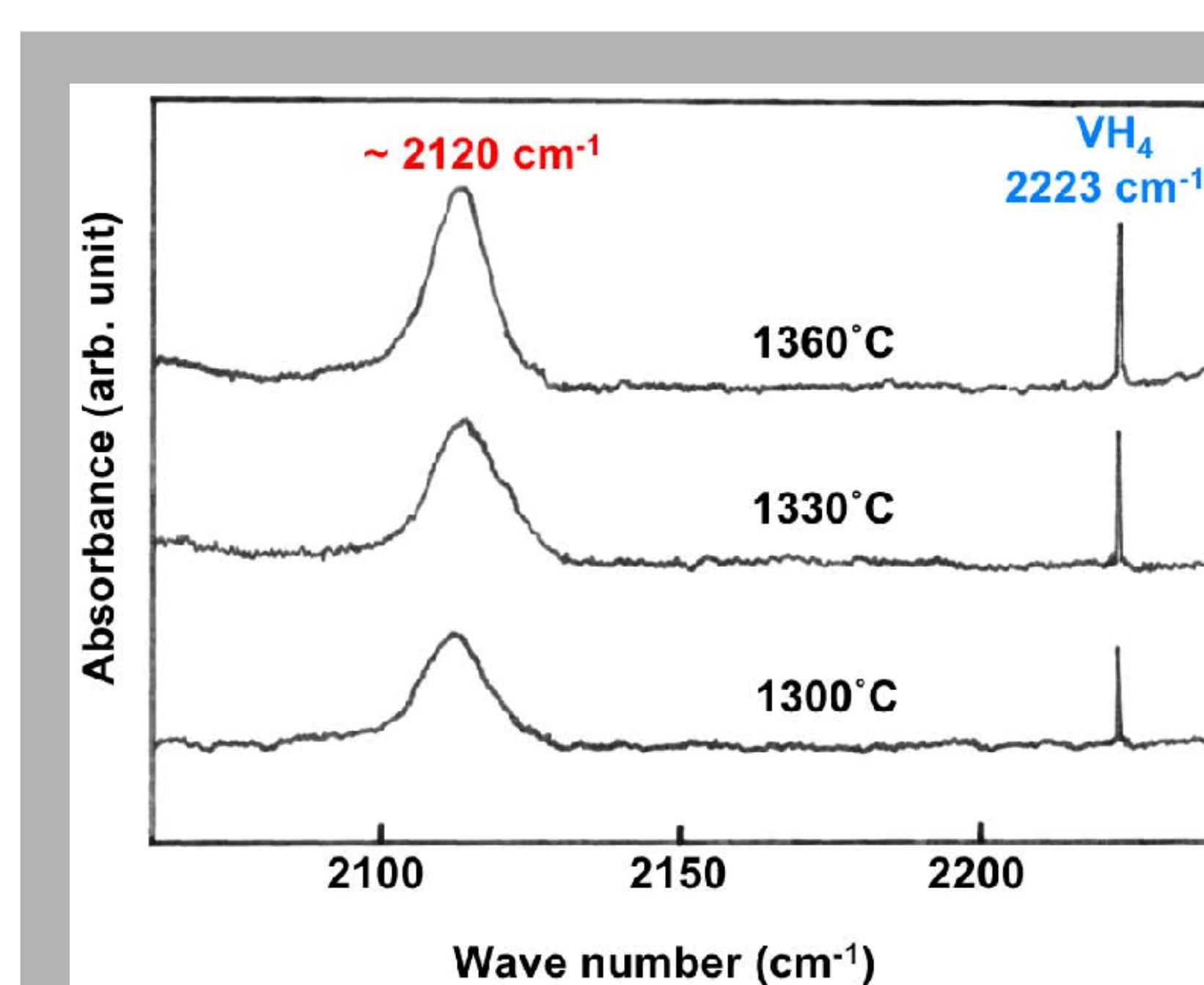
The vacancy concentration in an oxygen doped Si is indeed given by:

$$C_v = (1 - ZC_o) \exp(-G_o/kT) + ZC_o \exp\{-(G_o - E_b)/kT\},$$

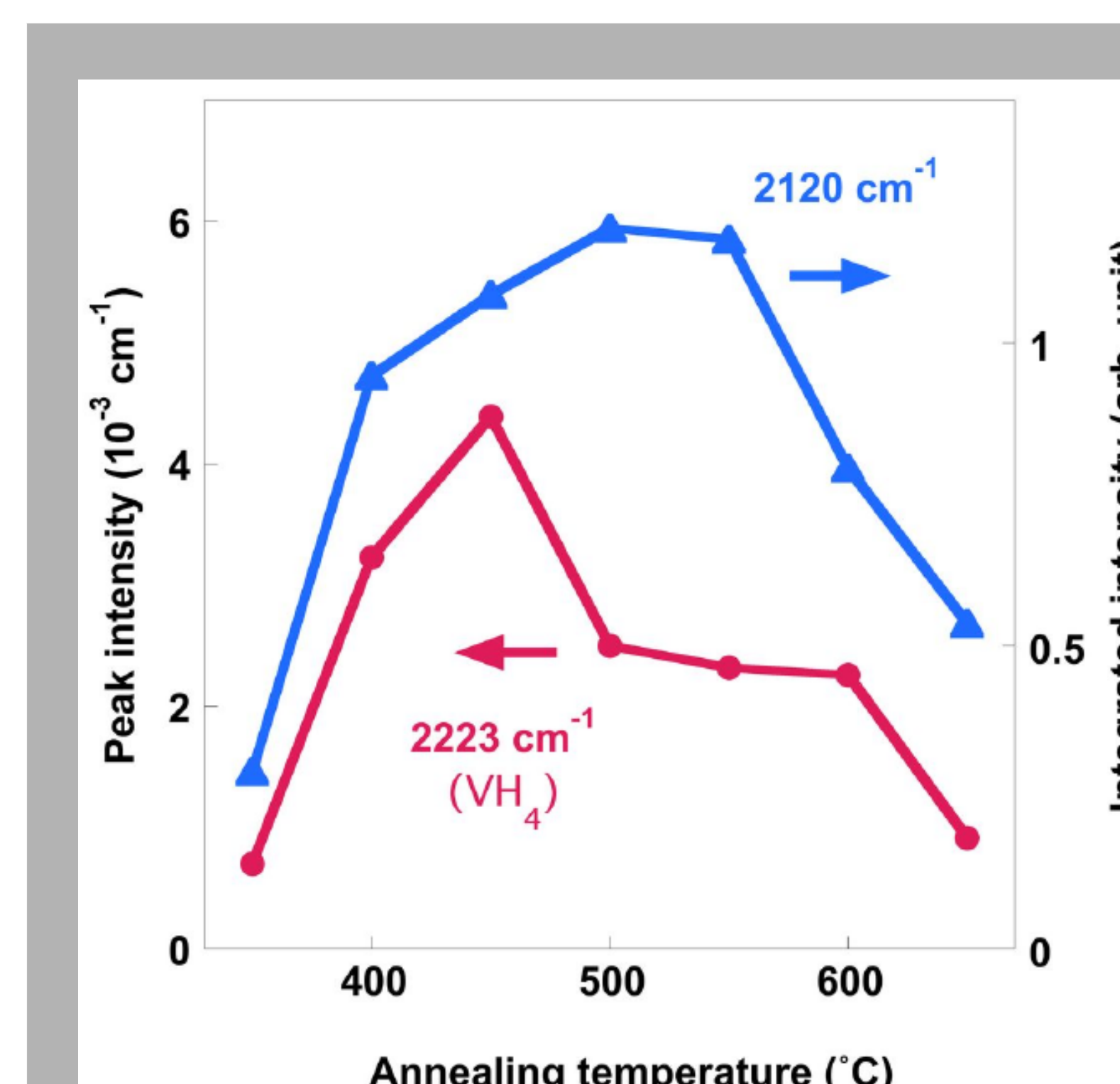
with  $C_v$  the total vacancy concentration,  $Z$  the coordination number,  $C_o$  the impurity concentration, and  $G_o$  the Gibbs free energy for vacancy formation in the perfect crystal part.  $k$  is the Boltzmann constant.  $E_b$  is the interaction energy. For oxygen  $ZC_o \ll 1$  so that the total vacancy concentration increases with oxygen concentration (3).

After taking into account the contribution from vacancies generated in a perfect crystal, the formation energy of a vacancy at an oxygen atom was evaluated to be about 1.5 eV.

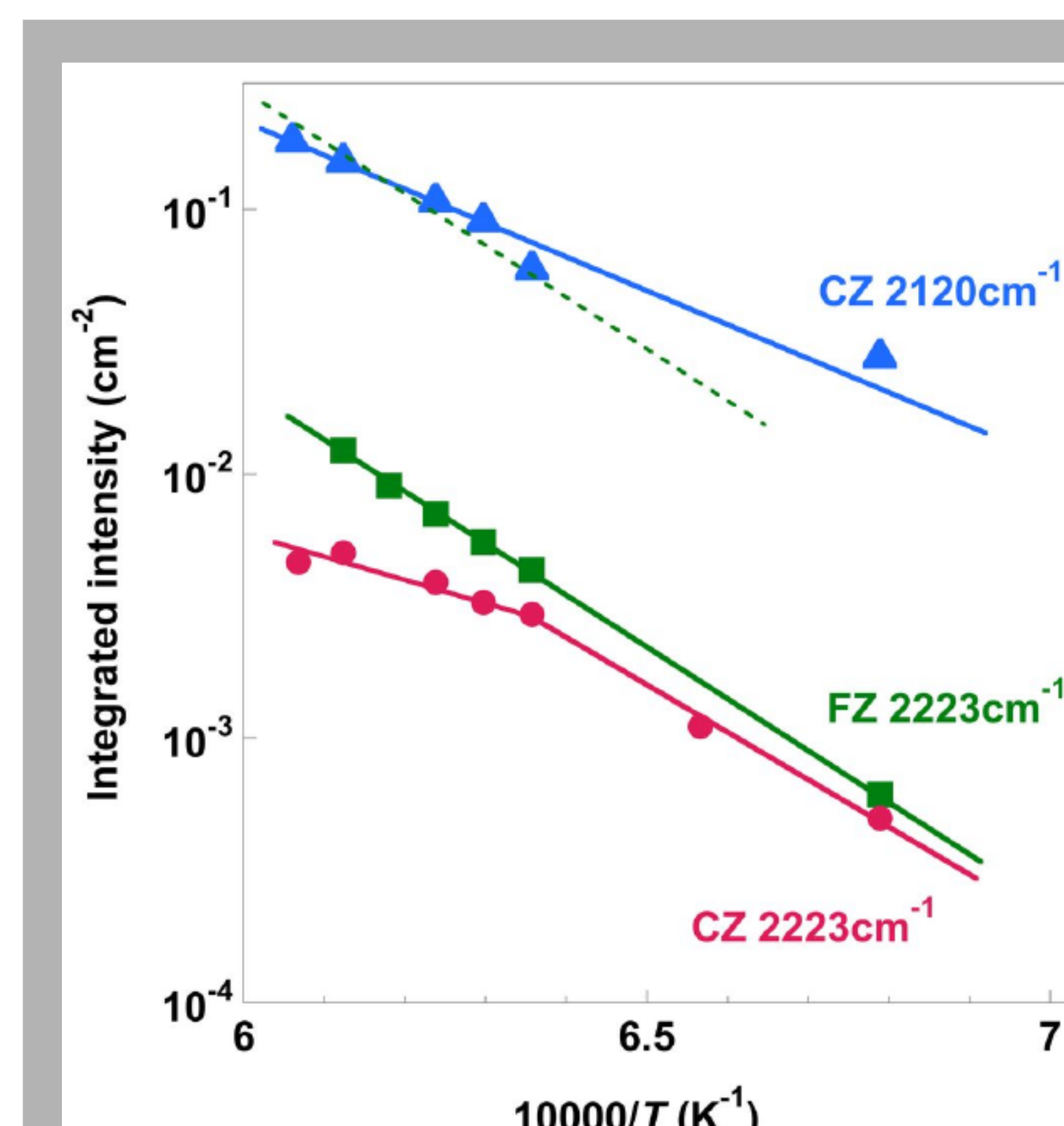
A similar reduction of the apparent vacancy formation energy and also a higher vacancy concentration than in FZ Si at high temperatures was observed in Ge doped Cz-Si (5).



**Fig. 1.** FTIR absorption spectra of CZ Si samples quenched from different temperatures (3).



**Fig. 2.** Isochronal annealing temperature dependence of the peak intensity of the  $2223 \text{ cm}^{-1}$  peak and the integrated intensity of  $2120 \text{ cm}^{-1}$  peak of a Cz Si specimen. The specimen was quenched from  $1364^\circ\text{C}$  and then annealed during 30 min at each temperature.



**Fig. 3.** Quenching temperature dependence of the integrated intensities of the  $2223$  and  $2120 \text{ cm}^{-1}$  peaks.

## Acknowledgments

The authors acknowledge the Advanced Research Center of Metallic Glasses of IMR for using the FTIR equipment. M. Suezawa is grateful to Covalent Silicon Co. Ltd. for financial support. J. Vanhellemont is indebted to JSPS for his fellowship as visiting professor.

## References

- (1) N. Fukata, A. Kasuya, and M. Suezawa, *Jpn. J. Appl. Phys.* **40** (2001), p. L854.
- (2) H. Bracht and A. Chroneos, *J. Appl. Phys.* **104** (2008), Art. No. 076108.
- (3) M. Suezawa, N. Fukata, J. Vanhellemont and I. Yonenaga, submitted for publication.
- (4) V. V. Voronkov and R. Falster, *J. Electrochem. Soc.* **149** (2002), p. G167.
- (5) J. Vanhellemont, M. Suezawa and I. Yonenaga, *J. Appl. Phys.* **108** (2010), Art. No. 016105.