Silicon Carbide Polytypes and Thermal Pase Transformation

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Abstract

The structure of Silicon carbide (SiC) was reviewed in the lights of the polytypism. It is found hexagonality can be used to identify the unknown SiC polytypes. Thermal phase transformations from cubic SiC to hexagonal SiC and vice versa under high temperature are understood with their applications in polytype-controlled epitaxial growth.

Silicon carbide is by far the most widely investigated among polytypic substances because it was, for a long time, the only substance known to be polytypic and it exhibits the large number of beautifully odered modifications. Lately it has also received considerable attention on account of its increasing technical and industrial inportance.

1 SiC polytypes and the structures

Silicon carbide(SiC) shows polytypism which takes a close-packed structure with the various atom stacking sequences. It has numerous crystaline forms with the same chemical composition (each silicon atom is surrounded tetrahedrally by four carbon atoms and vice versa). More than 200 kinds of SiC polytypes have been reported. The structure of SiC polytypes can be viewed as stacking SiC double layers on top of one another along the c direction. To describe SiC polytypes, Ramsdell notation has been used which shows the number of layers in the unit cell followed by the lattice type H, R or C. Thus a symbol nH represents a structure with an n-layered repeat period along the c direction and a primitive hexagonal lattice while $3mR$ denotes a structure with a $3m$ layered repeat period and a primitive rhombohedral cell. And 3C-SiC is the ony cubic modification which has a zinc-blende structure. Lattice structures of three dominat polytypes are shown below.

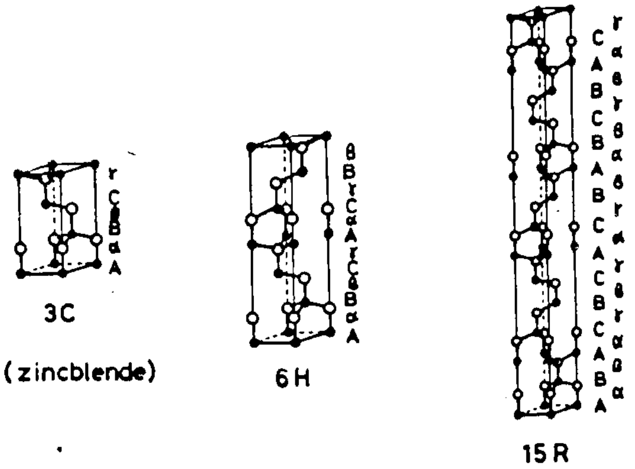

Figure 1: *Structure of SiC. Si and C atoms are notated by large open and small solid cicles, respectively.*

2 Semiconduting properties

All SiC polytypes have indirect band gaps (E_{Gx}) and release exitons which subsequently decay by photon and phonon emission (Fig.2). Some of the SiC polytypes show superior electrical properties as wide-gap semiconductors. 3C-SiC has a wide band gap (2.2 eV at room temperature), high electron mobility (1000 $\mathrm{cm}^2/(V \cdot s)^2$) and high electron drift velocity ($2.4 \sim 2.7 \times 10^7$ cm/s in the $1 \sim 2 \times 10^5$ V/cm range) [1][2] and is recognized as a promising polytype for high-temperature, high-power and high-frequency operation of devices. And 6H-SiC with a band-gap of 2.86 eV is promising in blue light-emittng diode(LED) application because both p- and n-type conduction can be easily obtained by impurity doping compared with other candidate materials such as ZnS, ZnSe and GaN.[3] But because of difficulty in producing large-area single crystals of 6H-SiC, the development of such electronic devices has been delayed.

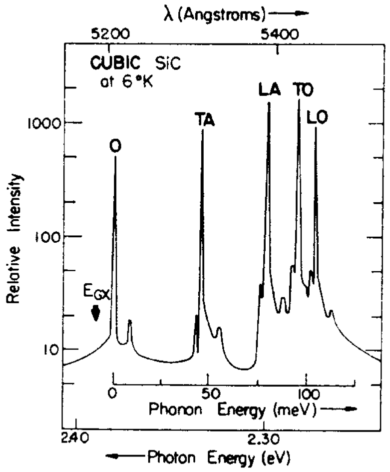

Figure 2: *The luminescene spectrum of four-particle nitrogen-exiton complexes in cubic SiC at 6°K. The phonon-free line is labeled* **0** *and its energy is used as the zero for the upper "phonon energy" scale, from which one may read directly the energies of TA, LA, TO, and LO phonons. The 10 meV between* E_{Gx} *and* **0** *is a measure of the binding energy of the exiciton to the nitrogen atom.*

3 Hexagonality and polytype identification

In the structure analysis of SiC polytypes X-ray diffraction method has widely been used, in which postulated possible layer sequences are compared with the theoretical intensities of possible structures for best fit.[4] But for long-period polytypes, hexagonality is used as there are relationship between the hexagonality and the physical quantities such as band-gap energies and phonon properties.[5][6]

Polytype	Exiton energy gap, E_{Gx}	hk notation	hexagonality
3C	2.390	*k*	0
8H	2.80	*hkkk*	0.25
21R	2.86	*hkkhkkk*	0.29
15R	2.986	*hkhkk*	0.4
33R	3.01	*hkkhkkhkkhk*	0.36
6H	3.023	*hkk*	0.33
4H	3.263	*hk*	0.5

Hexagonality is defined as $\sigma = \rho_h/(\rho_h + \rho_k)$ where ρ_h and ρ_k are numbers of layers in a hexagonal or cubic environment, respectively, which are determined depending on whether the relative orientation of atoms in the two neighboring planes is that found in hexagonal(h) or zinc-blende(k) lattice. Table 1 shows the hexgonalities of several SiC polytypes with E_{Gx} at 4°K.

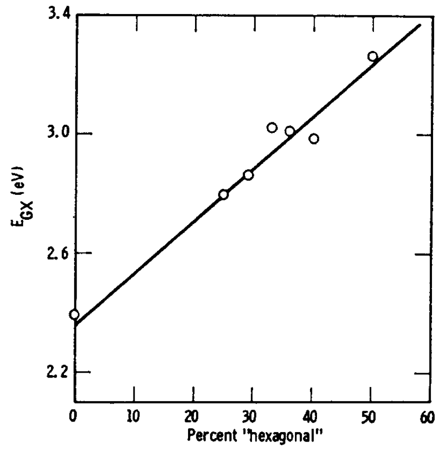

Figure 3: *A plot of E_{Gx} versus hexagonal(%).*

A plot of E_{Gx} against hexagonality is shown in Fig. 3 indicating a roughly linear relationship.[5] And Nakashima *et al.* obtained the correlation between hexagonality and two transeverse optical phonon mode ($\omega(E_t)$ and $\omega(A_{1t})$) spliting frequency which is given by

$$\Delta\omega = \omega(E_t) - \omega(A_{1t}) = 29.4\sigma(cm^{-1})$$

where σ is the hexagonality.

4 Thermal phase transformation

The most of the SiC polypypes are thermally very stable up to 2000°C but some of them are unstable at such high temperatures and transform to more stable polytypes. The 2H $\rightarrow$ 3C, 2H $\rightarrow$ 3C $\rightarrow$ 6H, 2H $\rightarrow$ 6H and 3C $\rightarrow$ 6H phase transformation at high temperatures have been proposed.[7][8] Two kinds of mechanisms for phase-transformation were suggested. [7] One is the idea of transformation via the vapor phase in which crystals are vaporized at first and then high temperature polytypes are formed by recrystallization from the vapor.

The other idea is the solid-state phase transformation by rearrangement of atoms such as the layer displacement caused by the nucleation or propagation of stacking faults.[8][3] Table 2 is showing the rate of transformation of 2H $\rightarrow$ 3C and 3C $\rightarrow$ 6H from Ref.[8].

.... 2H $\rightarrow$ 3C			3C $\rightarrow$ 6H....................................		
Temp. (°C)	Time (hr)	% 2H	Temp. (°C)	Time (hr)	% 3C
1600	1	74	1600	504	100
1600	2	60	1700	233	100
1600	3	48	1800	114	75
1600	3.5	38	1900	65.5	65
1600	6	8	2300	1	50
1600	7	1	2300	15.5	0

If one can control atomic arrangements of the surface of 3C-SiC to 6H-SiC by temperature, 6H-SiC will be grown on 3C-SiC substrate which will make it possible to grow large size crystals of 6H-SiC.

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