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Correlation between layer thickness and periodicity of long polytypes in silicon carbide

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Abstract
The layer widths and repeat spacing of long-period polytypes (LPP's) have been determined using synchrotron radiation source (SRS) X-ray diffraction topography (XRDT). This method has proved to be a powerful tool in investigating the spatial extent of one-dimensional disorder (1DD), long-period polytypes (LPP's) and the boundaries of polytype layers in silicon carbide (SiC). The resulting neighbourhood coalescence models have confirmed the validity of the sandwich rule even in the limit of two arbitrarily long LPP's, as well as the unique nature of the 6H polytype. A significant empirical trend is reported here that relates the thickness of LPP layers to the periodicity of the repeat stacking sequence measured on the topographs. A good correlation between the data suggests that this behaviour is governed by a simple mathematical expression $t = kN^n$. Values for k and n have been determined that relate the polytype thickness (y in microns) to the number of hexagonal layers (x) in the polytype stacking repeat.

Keywords: A. Semiconductors B. Crystal growth C. X-ray diffraction

1. Introduction

1.1. Modern semiconductor with an age-old stacking problem

It is well known that silicon carbide is of great interest to the aerospace and power generation industries for opto-electronic, high-temperature, robust ambient and chemically aggressive environment applications Zimmermann 2002 [1], tCore 2002 [2]. In fact the material constitutes a semiconductor family, Camassel et al. 2001[3] of different polytypes with the potential to significantly impact the wide band gap market, earning it the sobriquet "semiconductor of the 21st century". Commercially the manufacture of large single wafers and devices is dogged by the presence of micropipe defects while academically the nature of the phenomenon of polytypism is still of interest. The ability of SiC to form so many polytypes is well documented

Kelly et al. 2001 [4] and despite the discovery of the many (*poly*) different layer-stacked types (*typie*) by Baumhauer 1912 [5] ninety years ago, which he christened *polytypie*, a full explanation for their existence still remains elusive today.

The problem is essentially that the one-dimensional ordering arrangement in SiC has produced over 150 different layer periodicities based on the simple ABA… ABC… stacking sequences found in close packed structures, Trigunayat and Chadha 1991 [6]. This arises from the large number of possible repeat sequences, the largest reported spacing in SiC being 3015 Å, Mitchell 1954 [7]. Besides these long period ordered structures one-dimensional disorder, when there is no finite lattice repeat, is also a prevalent feature in silicon carbide.

Recently there has been renewed interest in the interface between polytypes in syntactic coalescence; historically the term was first used by Ungemach 1935 [8]. The boundaries between polytypes have become a region of genuine interest since the discovery by Barnes et al.1991 [9] of thin ($\leq$ 5 μm) one-dimensionally disordered (1DD) layers in silicon carbide (SiC) crystals. With the advent of synchrotron radiation source X-ray diffraction edge topography (SRS-XRDET) and the improved resolution available from later generation machines, it has become possible to unlock the secrets of polytype coalescence.

2. Experimental

2.1. Unlocking the secrets of polytype coalescence

The methodology in producing polytype models, which retain morphological fidelity, is now routine and has resulted in a quite unprecedented database Kelly 2002 [10] detailing the spatial extent of polytypism in silicon carbide. Features, which are quite common in the models, include the presence of defect bands in central $52\bar{7}0$

reflections, thin one-dimensionally disordered (1DD) layers and long-period polytypes (LPP's) all of which have been previously discussed by the authors, Kelly et al. 1995 [11].

As an example of the determination of a long-period repeat Figure 1a shows a full plate topograph, with the closely spaced reflections reminiscent of a polytype with a large repeat spacing. Figure 1b shows a magnified section of the region in 1a with the LPP layers clearly marked A – B, while Figure 1c shows a model of the polytype content of the crystal. The LPP obeys the sandwich rule, Fisher and Barnes 1990 [13], in which LPP layers are found sandwiched between their shorter period (6H, 15R and 4H) counterparts.

3. Results

3.1. The boundary of Long Period Polytype environments

The width of the polytype layer shown in Figure 1b (which was determined to have a repeat spacing of 201H/603R) was measured as 20 μm, Kelly et al. 2001[4]. Similar results have been obtained in all for 25 LPP's, where care was taken to note the immediate adjacent polytype layers on either side of the LPP. One can differentiate three different environments for any individual LPP layer:

- one in which the adjoining layers are common low period polytypes, typically 6H + LPP + 6H (or e.g. 15R/8H),

- where one of these neighbouring layers is disordered an example such as 6H + LPP + 1DD is the usual model,

- where the LPP abuts the outer edge surface of the crystal, the other neighbour being disordered e.g. 1DD + LPP + ---.

All of the data, Kelly et al. 2001 [4], fit into one of these three regimes and subsequently a plot of the widths of the LPP layers (µm) against the number of layer repeats has produced an interesting trend.

There is the same overall shape for the 3 different regimes. In each of the cases, shown in Figure 2 a-c, there is a decrease in the width of the LPP layer corresponding to an increasing period repeat of the number of layers in the polytype. Simply put, as the polytype repeat gets longer it cannot grow so much. This implies that the field of stable growth decreases sharply with polytype repeat order.

4. Discussion

4.1. When does an LPP become a 1DD layer ?

It is an easy matter to fit a trend line for each of these graphs, the result of which is that they can be described by the general equation $t = kN^n$. Values have been determined for the constant k and exponent n and these are tabulated in Table 1.

Table 1. Parameter values to fit $t = kN^n$.

LPP regime	k	n
6H + LPP + 6H	645.5	– 0.73
6H + LPP + 1DD	739.1	– 0.84
1DD + LPP + ---	3903.1	– 0.95

Combining these values leads to an expression that relates the LPP thickness (t in µm) to the polytype spacing (N in number of hexagonal layers) which can be generally written as:

$$t = 700 \, N^{-0.8} \qquad\qquad \textbf{1.1}$$

Is it possible that such a simple expression can herald the onset of the transition from an ordered (albeit a very long period) structure to disorder. It is an interesting thought to speculate on the width of a layer as the polytype spacing increases indefinitely.

The indication from the data in Table 1 is that the constant k (measured in μm per hexagonal layer) increases as the LPP tends more towards a disordered environment. In the limit is it reasonable to assume that the LPP approaches a 1DD layer and if so an intriguing question still remains "When does a long-period polytype become a one-dimensionally disordered layer?" As Mitchell 1954 [7] said "With the discovery of each new polymorph of silicon carbide it becomes more evident that there is no limit to the possible modifications of this substance…". It is now timely to revisit this statement in the light of the data presented here.

4.2. Is there an ideal thickness for the ordered 6H structure?

One might now speculate on the implications of the KFB equation. This equation can be viewed simply as an empirical statement of the optimum thickness for different polytypes, without giving any actual reasons for this (such as the balance of bulk and surface free energies). The equation as stated will only be appropriate to the range of growth conditions encountered in the study: If other growth modes were included this would bias the equation towards different parameters and the scatter of data points would increase; conversely, more specific growth conditions would segment the dependency and reduce the scatter (as clearly occurs in Table 1; Fig.2;). In this context the equation indicates that the growth rate for a given polytype will only be significant while its thickness approaches the value t (μm) and then one of two things happens: either (i) the growth rate slows down (or stops), or (ii) an alternative, faster growing, polytype growth becomes more favourable. Our previous observations suggest that for (ii) to occur an intermediate transitional layer is required.

Against this background one might ask the question, what are the limits on polytypism suggested by the KFB equation? If we insert the value N=6 for the most common polytype, the 6H, the equation returns a thickness value of ~200 μm which naturally corresponds to the mean of our observations; this is as one would expect. But what do we get if we insert a value for N corresponding to the *longest* polytype encountered in this study? Kelly 2002 [10] has been able to measure an hexagonal repeat of 474H. Substituting this value into the KFB equation returns a thickness t of ~5 μm, an intriguing result in view of the fact that 5 μm also corresponds to the thinnest 1DD layers observed previously, Barnes et al.1991 [9]. It is believed that highly defective 1DD (or very long repeat polytype) layers act as transitional layers to accommodate the discontinuity between two different adjacent polytypes. Their fineness might be considered as a further expression of the trend given by the KFB equation. That is, fine 1DD layers represent the extent of disorder required to accommodate the discontinuity between adjacent polytypes.

5. Conclusion

5.1. Is there a limit to polytypism in SiC?

However the more intriguing question to pose is whether the KFB equation implies a limit to the number of polytypes that can exist in practice. We can test this idea by asking what is the longest polytype period (i.e. largest N) that the equation predicts. As N increases the polytype width decreases, so if continued indefinitely there would come a point when the width approaches the unit cell c-dimension. For the purpose of order of magnitude calculations we might put the limiting width value for this as two unit cells ($t \rightarrow 2c$), simply to represent the most basic, singly repeating, polytype "crystal". However the unit cell c-spacing is also N times c_o, the SiC h.c.p. repeat

distance (2.513 Å), so substituting these relations for t and c into the KFB equation gives:

$$t = 2c = 2Nc_o = kN^n$$

which re-arranges to give a solution for N:

$$N = (2c_o/k)^{1/n-1}$$

and returns limiting values of N~2,600 and t~1.3 μm on inserting the above values for c_o, k and n. This is consistent with observations so far: the longest hexagonal repeat reported to date is N=1,200 Mitchell, 1954 [7]. Presumably as N approaches the 1000 region there is an increasingly smaller drive to form ordered polytypes over the disordered form. Any ordered manifestation of longer polytypes would exist with thicknesses of ~1 μm or less, which would be on the limit of observation by X-ray topography with current third generation synchrotron sources. Thus the prediction given here, that silicon carbide polytypes will not be found with c-repeats greater than, say, 2600 layers, is just within range of verification by experiment.

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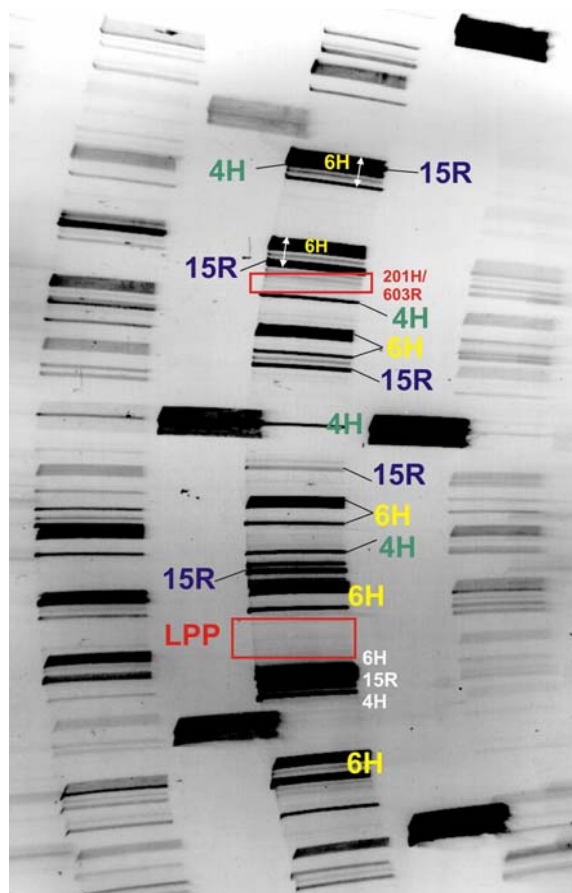[13] Fisher G.R., Barnes P. (1990) Phil. Mag. **B61**, 217-236.

Figure Captions

Figure 1 Sample J105 containing a long-period polytype 201H/603R that has been previously observed by Kuo Chang-Lin 1965 [12].
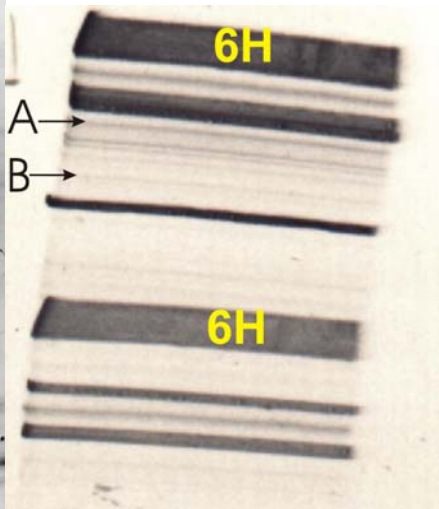
    (a)   Polytype contributions displaced along the diffraction row with LPP spacings and 1DD visible.

    (b)   The region labelled A-B contains 6 LPP repeats corresponding to a period of 201H. The 6H period is shown for comparison. The section of reflections A-B is from the area labelled 201H/603R. The area around this label represents the enlarged section shown in b. Measurements were made from several regions containing LPP reflections to improve the accuracy in the determination of the LPP repeat, like those shown in the section labelled LPP to the lower part of a.

    (c)   A model to scale of the polytype content of the crystal. All long-period polytypes found in the survey are listed by Kelly et al. 2001 [4].

Figure 2 Long-period polytype layer widths (μm) displayed as a function of their corresponding repeat spacings. The LPP widths were measured directly from the photographic plates under microscopic examination. The polytype period repeat was estimated by comparing the LPP repeat spacing to that of the standard 6H spacing. When the data in Table 1 is classified according to the neighbourhood environment of the LPP, three separate models can be identified which show the same trend.

(a) The LPP can be identified as being sandwiched between the common basic 6H polytypes (or other short period repeat).

(b) One of the two adjoining neighbours is a disordered layer (1DD), in this case there is a rich display of behaviour.

(c) The LPP forms near the outer surface of the edge still clearly demonstrating behaviour similar to that in (a). In (a) the LPP forms in the bulk of the material as opposed to on the surface of the crystal as in c.

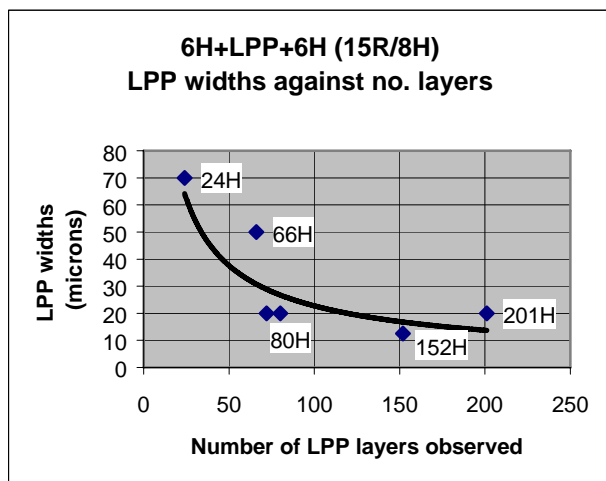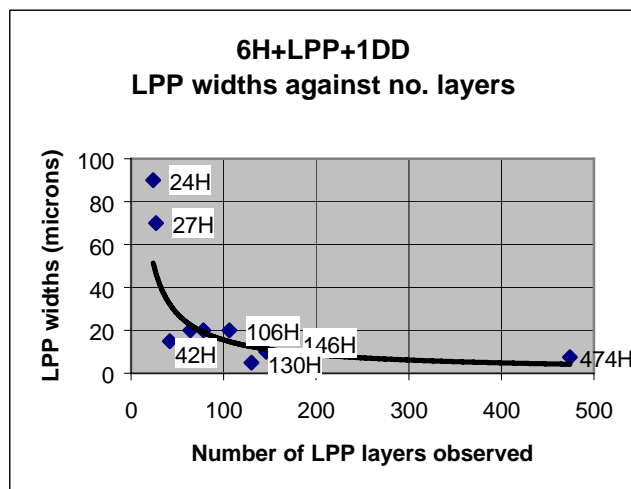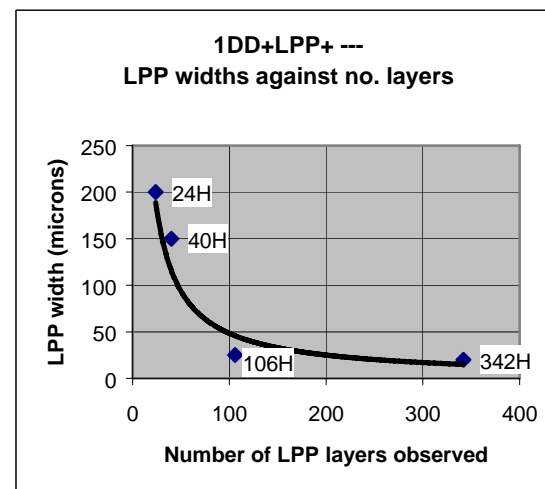(a)   (b)   (c)

Figure 1

(a)

(b)

(c)

Figure 2