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Crystallographic Match in Epitaxy between Silicon and Sapphire

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If silicon is assumed to occupy potential aluminum sites in epitaxy between silicon and sapphire, it is shown from a systematic analysis of certain dense atomic planes that approximate lattice matches between non-isomorphous silicon and sapphire can be found. The matching planes are (110) silicon on $(11\bar{2}0)$ sapphire, {100} Si on $(01\bar{1}2)$ sapphire, and {111} silicon on (0001) sapphire. Experimental investigation by others as well as in this laboratory confirms that when sapphire substrates are cut parallel to the planes listed, successful epitaxy is obtained.

Introduction

The epitaxic relationships between two crystals of the same material and between isomorphs are simple in that the matching planes usually have the same indices. Recently, however, epitaxy has been realized between non-isomorphous substances, in which case the epitaxic relationships are less obvious. While a similar atomic arrangement in certain planes of non-isomorphous lattices is quite possible, cases of epitaxy are reported (Barret, Miller, Pulliam & Warren, 1963; Manasevit & Simpson, 1964) where there is no match between the substrate surface plane and any deposit crystal plane. Instead, other planes in the substrate crystal match deposit planes, usually as inferred from pole coincidences in stereographic projections.

Since epitaxy between non-isomorphous substances is possible, the number of suitable materials for use as substrates is expected to increase considerably. It would therefore be of advantage to develop methods of identifying matching planes in non-isomorphous crystals. It is conceivable that mathematical and computer methods can be used to find such matches between any two crystals. Before such a general approach is taken, it would be of value to single out two well-known non-isomorphous structures where epitaxy has been demonstrated, and search for possible atomic matching planes, without reliance on experimental evidence. For this purpose silicon and sapphire were chosen. The analysis, as presented here, is based strictly on crystallographic relationships.

An experimentally determined epitaxic relationship between silicon and sapphire was obtained by Manasevit & Simpson (1964). After the present analysis was completed, two articles have appeared showing additional experimentally determined relationships, one by Manasevit, Miller, Morritz & Nolder (1965) and another by Joyce, Bennett, Bicknell & Etter (1965). Nolder & Cadoff (1965) analyzed the X-ray data of Manasevit *et al.* and demonstrated the degree of lattice match for the experimentally determined relationships. The results of these investigations in comparison with this analysis will be referred to in a later section.

Factors pertinent to crystallographic match

The type of bonding expected between silicon deposit and sapphire substrate determines what type of sapphire atomic planes should be selected for comparison with silicon planes. There are three types of atomic plane available in sapphire; some contain Al atoms only, others O atoms only, and still others both Al and O atoms. The O planes are always nearest-neighbor planes to the Al planes.

The viewpoint is taken here that the substrate surface plane contains oxygen atoms only. This is valid in a practical way, since an Al plane at the surface would immediately oxidize. The nearest parallel plane below it is an Al plane, and immediately above it would be another identical Al plane. The assumption is made, therefore, that epitaxic deposition of silicon on sapphire occurs as an entrance of Si atoms into sites which otherwise would be potential Al sites. Accordingly, Si atomic planes are compared with sapphire planes containing Al atoms only for matching purposes. That Si would primarily substitute into Al sites was also assumed by Nolder & Cadoff (1965) on slightly different grounds.

Since as little distortion as possible is desired in the first monolayers of deposit, two restrictions are put on the selection of matching planes. The first restriction is that the population density be high. If this is not high, Si atoms may deposit between Al sites in a disorderly manner, and several monolayers may have to grow before the normal Si structure is obtained. A second restriction is that the population density be the same and the symmetrical arrangement similar in the two planes being compared. This means a one-to-one correspondence between Si atoms and Al sites.

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Selecting dense Si and Al planes

Silicon has the diamond structure. It is cubic, $a=5{\cdot}431$ Å, with eight silicon atoms in the positions 8(*a*) of space group *Fd*3*m*. Three low-indexed, dense Si planes can be selected from this atomic arrangement: {100}, (110), and {111}, respectively. These planes are subsequently used for possible matching with dense Al planes in sapphire.

Sapphire, or α-Al_2O_3 (corundum), is rhombohedral with $a=5{\cdot}12$ Å, $\alpha=55°17'$, $Z=2$, space group $R\bar{3}c$ (Pauling & Hendricks, 1925). Referred to the hexagonal cell ($a=4{\cdot}75$, $c=12{\cdot}97$ Å), the twelve Al atoms lie in positions $12(c), 0, 0, z; 0, 0, \bar{z}; 0, 0, \frac{1}{2}+z; 0, 0, \frac{1}{2}-z$; with $z=0{\cdot}105$.

There are only two non-equivalent, dense Al planes parallel to **c**, here selected as $(\bar{1}010)$ and $(11\bar{2}0)$. Examination of the Al arrangement in these two planes shows that $(11\bar{2}0)$ is much denser than the other. This arrangement is shown in Fig. 1, where linear rows of Al atoms are inclined to the *c* axis and parallel to $[2\bar{2}01]$. Considering planes normal to the *c* axis, the Al arrangement parallel to the basal plane is typically hexagonal close packed and of sufficient density and order for matching purposes.

Since none of the *z* coordinates of Al are whole fractions of the *c* axis, it appears that no Al plane of simple indices inclined to **c** can be found. Al planes parallel to other planes of simple indices are found, however, which are already indicated in Fig. 1. This situation can be evaluated by projecting the Al atoms in the cell on $(\bar{1}010)$ and $(11\bar{2}0)$. This is exemplified in Fig. 2, where a projection along $[\bar{2}110]$ on $(\bar{1}010)$ is made. This is not a normal projection. An interesting puckered and dense arrangement is found parallel to $[\bar{4}8\bar{4}3]$. Because these Al atoms do not all lie exactly in a plane, this arrangement is not considered further. Al planes are found to lie parallel to $[2\bar{4}23]$, which should be a fairly dense arrangement. These Al planes are parallel to $(01\bar{1}2)$ and are drawn in Fig. 3.

Search for other dense planes resulted only in planes equivalent to those selected. In summary, the three dense, non-equivalent Al planes selected for matching purposes are $(11\bar{2}0)$ (Fig. 1), plane parallel to (0001), and plane parallel to $(01\bar{1}2)$ (Fig. 3).

Discussion

Matching the three Si and Al planes selected in the previous section, the fits shown in Figs. 4, 5, & 6, and in Table 1, are found.

Table 1. *Matching planes of silicon on sapphire*

Matching planes Si/Al	Quality of match	Misfit per Si unit mesh	Fig.
$(110)/(11\bar{2}0)$	Good	5 %	4
$\{100\}/(01\bar{1}2)$	Good	6 %	5
{111}/(0001)	Fair	15 %	6

The average displacement of the center of the Si atom from the center of the Al atom over four Si meshes for $(110)/(11\bar{2}0)$ is about 0·55 Å. From this the linear misfit per Si mesh is estimated to be about 5% within an area of four meshes. For $\{100\}/(01\bar{1}2)$ the displacement is about 0·65 Å over six Si meshes, or a linear misfit per Si mesh of about 6%. The average displacement for {111}/(0001) is about 0·80 Å over about one unit mesh or a linear displacement of about 15%.

In Figs. 4 and 5 the unit mesh of the Si net is slightly larger than that of the Al net. If nucleation were to occur at only one point, complete mismatch would soon occur as the deposit grows laterally. Examination of the growth mechanism (Manasevit *et al.*, 1965) shows, however, that nucleation occurs at numerous points simultaneously, the various deposit areas will merge, and gross mismatch in large areas is minimized.

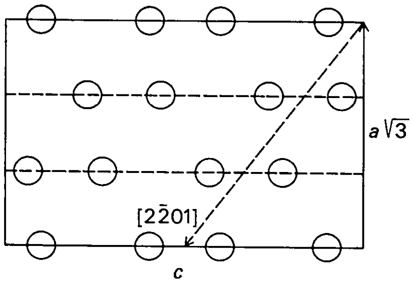

Fig. 1. Al arrangement in $(11\bar{2}0)$.

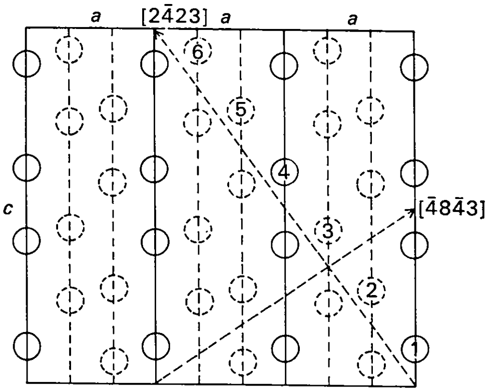

Fig. 2. Projection of Al atoms along $[\bar{2}110]$ on $(\bar{1}010)$. (Not a normal projection.)

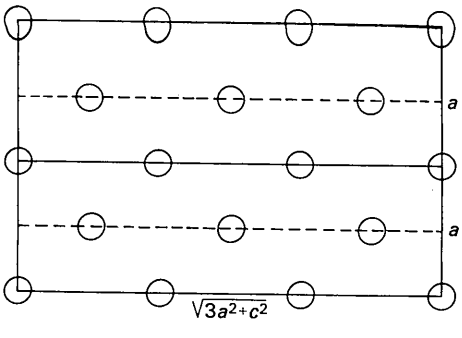

Fig. 3. Al arrangement in plane parallel to $(01\bar{1}2)$.

Further, the compressibility of silicon (Bridgman, 1958) will slightly counteract the increased tendency of mismatch in lateral growth.

From the above analysis, it would appear that sapphire surfaces cut parallel to (11$\bar{2}$0) and (01$\bar{1}$2) would be good substrates for epitaxic deposition of silicon.

While the above matches were based solely on an analysis of the silicon and sapphire lattices, comparison is now made with experimentally determined relationships and matches determined in other laboratories as well as a preliminary result from this laboratory. Manasevit and Simpson (1964) deposited silicon on a sapphire substrate parallel to (11$\bar{2}$3)*. No simply indexed Si plane can be found which will match (11$\bar{2}$3) sapphire. Their pole figure of the deposited substrate revealed no Si plane parallel to (11$\bar{2}$3) but showed that (110) silicon was parallel to (11$\bar{2}$0) sapphire. This tends to agree with the match presented here in Fig. 4. Joyce *et al.* (1965) also refer to (110) silicon parallel to (11$\bar{2}$0) sapphire. While the substrate in this case apparently was cut parallel to (11$\bar{2}$0), it is not clear what was inferred, since they later state that 'for silicon on (11$\bar{2}$0) alumina surfaces, there appears to be no atomic fit which gives the necessary epitaxial arrangement ...'.

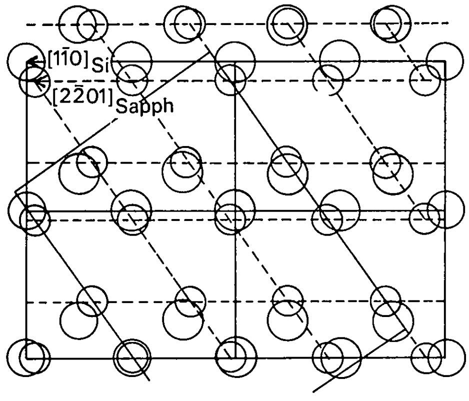

Fig. 4. (110) Si on (11$\bar{2}$0) Al.

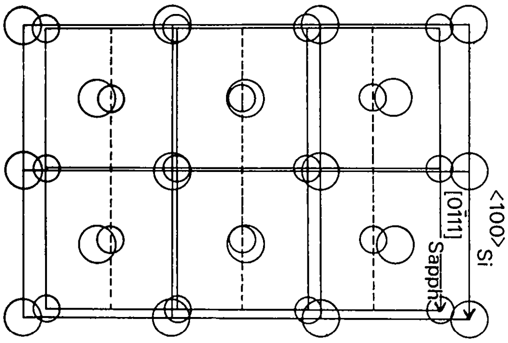

Fig. 5. {100} Si on Al-plane parallel to (01$\bar{1}$2).

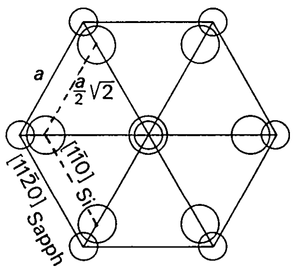

Fig. 6. {111} Si on Al-plane parallel to (0001).

Manasevit *et al.* (1965) show experimentally that (111) silicon is parallel to (11$\bar{2}$0) sapphire if sapphire is cut parallel to (11$\bar{2}$0). Nolder & Cadoff (1965) analyze this further and present the degree of match (their Fig. 9). It is difficult to justify any match between these two planes, and a poor match is also reported by Nolder & Cadoff. The only good match found for (11$\bar{2}$0) in this study is (110) Si (Fig. 4).

To clarify experimentally the (110)/(11$\bar{2}$0) match, a preliminary experimental examination was made in this laboratory. The silicon deposit was of proper thickness to show both the Si and α-Al_2O_3 Laue spots, as taken with the X-ray beam normal to (11$\bar{2}$0). A single-crystal silicon deposit was indicated. While not all the silicon reflections showed up on the photograph, those which did show up agreed with the Laue pattern obtained normal to (110) of silicon.

Manasevit *et al.* (1965) determined experimentally the relationship (001) silicon on ($\bar{1}$012) sapphire. On this basis Nolder & Cadoff (1965) illustrated the corresponding match (their Fig. 4) and term it a good one. This match is equivalent to the one in Fig. 5.

The same authors also find the relationship (111) silicon on (0001) sapphire with [1$\bar{1}$0] silicon parallel to [$\bar{1}\bar{2}$30] sapphire, and Nolder & Cadoff (1965) illustrate the match (their Fig. 7). These planes are identical with the two planes matching in Fig. 6, but the directional alignment is different.

Finally, Manasevit *et al.* (1965) and Nolder & Cadoff (1965) determine the epitaxic relationship (111) silicon on (11$\bar{2}$4) sapphire, and Joyce *et al.* find {001} silicon to be parallel to (0001) sapphire. The match (111)/(11$\bar{2}$4) is termed a poor one, and the Si and Al atoms do not show a one-to-one correspondence. The (11$\bar{2}$4) plane was not selected in this study because of its low atom density. It must be said that there is a certain similarity in the symmetrical arrangement of Si in {001} and Al in (0001), but the match is not a good one.

In the studies by Manasevit *et al.* (1965) and Joyce *et al.* (1965) pole coincidence in stereographic projections of silicon and sapphire was used to indicate which planes were parallel to each other. A note of caution is in order in this respect. While pole coincidence is necessary for lattice match in epitaxy, it is not sufficient proof for actual epitaxic contact between the two planes. It only proves that the planes are parallel. Epitaxic contact between planes not involving the sapphire substrate surface plane can be explained if

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* The authors call this the (22$\bar{4}$3) plane, but they had chosen a hexagonal cell with *c* one-half of the value chosen here.

atomic steps were present on the substrate surface or if silicon diffused below the surface.

In conclusion, approximate crystallographic match between the three pairs of atomic planes (110)/(11$\bar{2}$0), {100}/(01$\bar{1}$2), and {111}/(0001) in non-isomorphous silicon and sapphire has been found by systematic analysis of their lattice structures. The latter two matches agree with those of Nolder & Cadoff (1965). The same two matches have been experimentally verified by Manasevit *et al.* (1965). Parallelism between (110) silicon and (11$\bar{2}$0) sapphire has been experimentally verified by Manasevit & Simpson (1964) and by Joyce *et al.* (1965), but the first authors used a substrate which was not cut parallel to (11$\bar{2}$0), and the second authors reported no atomic fit between these two planes. Preliminary work in this laboratory, however, indicated epitaxy between (110) silicon and (11$\bar{2}$0) sapphire when sapphire was cut parallel to (11$\bar{2}$0).

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The Shape of Two-Dimensional Carbon Black Reflections*

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A rigorous derivation is given for the shape of a two-dimensional *hk* reflection for a turbostratic structure in which the layers are considered to be disks of radius R. An average disk dimension is defined as $L_a=(\pi/2)R$, and this dimension is obtained from the half maximum breadth of an *hk* reflection by $L_a=1\cdot77\lambda/(B\cos\theta_0)$. The constant differs by only 4% from that obtained in an earlier approximate treatment. This definition of an average dimension differs by 17% from that which has been used in recent treatments of carbon black patterns by the general Debye scattering equation.

Introduction

Carbon black is a common example of a turbostratic structure. Parallel layer groups are built up out of graphite layers, arranged parallel to one another, but with random orientation about the normal to the layers. Except for crystalline $00l$ reflections, the random orientations of the layers prevent the appearance of the general *hkl* reflections. The individual layers diffract independently, and we have two-dimensional *hk* reflections. For such a turbostratic structure, the reciprocal lattice comprises $00l$ points and continuous *hk* rods. In a powder pattern, the $00l$ points give the usual powder pattern peaks, and the *hk* rods give peaks which rise sharply on the small angle side and tail off slowly on the high angle side. From the shape of such a two-dimensional reflection, it is possible to obtain the size of the individual layers.

The problem of a two-dimensional powder pattern reflection from carbon black has been treated by Warren (1941). The graphite layers were assumed to be parallelograms of edges N_1a_1 and N_2a_2, where a_1 and a_2 are the usual graphite axes. An average dimension L_a was defined in such a way that for $N_1a_1=N_2a_2=Na$, the dimension is given by $L_a=(\sqrt{3}/2)\,Na$. Approximating functions of the type $\sin^2 Nx/\sin^2 x$ by Gaussian functions, the layer dimension L_a was expressed in terms of the breadth at half maximum intensity by the relation

$$L_a=\frac{1\cdot84\lambda}{B(\frac{1}{2},2\theta)\cos\theta_0}\,. \quad (1)$$

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