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(54) IMPROVEMENTS IN AND RELATING TO CRYSTALS AND THE MANUFACTURE THEREOF

(71) We, MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD, a Japanese body corporate of 1006 Oaza Kadoma Kadoma-shi, Osaka-fu, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to crystals and the method of manutacture thereof.

According to the invention, there is provided a method of manufacturing a single crystal device comprising the steps of providing on one major surface of a crystal substrate a three dimensional configuration of predetermined geometry, maintaining the substrate at a crystal growing temperature, directing at least one molecular beam from source means onto said substrate at an oblique angle relative to the major surface of said substrate and providing an environment between the source means and the substrate in which the mean free path of the molecules in the or each said molecular beam is greater than the distance between the molecular beam source means and said substrate, whereby to effect an epitaxially grown crystal layer in discrete local regions of said major surface of the substrate depedent upon the local arrival rates of said molecular beams at the major surface.

According to the invention there is further provided a method of manufacturing a single crystal device the method comprising the steps of forming on one major surface of a crystal substrate a three-dimensional configuration of predetermined geometry, maintaining the substrate at a crystal growing temperature directing at least one molecular beam from source means onto the substrate at an oblique angle relative to the major surface of said substrate, and providing an environment between the source means and the substrate in which the mean free path of said molecules in the or each said molecular beam is greater than the distance between the source means and said substrate, whereby to effect an expitaxially grown crystal layer in discrete local regions of said major surface of said crystal substrate separated from one another due to the variation in the local arrival rates of said molecular beams brought about by the predetermined geometry of the configuration.

Crystal devices and their methods of manufacture embodying the invention, will now be described, by way of example, with reference to the accompanying diagrammatic drawings in which:

Figure 1 is a perspective view of crystal growing apparatus embodying the invention;

Figure 2 is a perspective view of and fragmentary sections through a crystal substrate on which expitaxial growth is to be performed to provide one of the crystal devices;

Figure 3 is a fragmentary cross-section through the crystal device of Figure 2 during an epitaxial growth process;

Figure 4 is a graph of arrival rate versus distance for the epitaxial growth on the crystal device of Figure 3;

Figure 5 is a section through the crystal device of Figure 3 illustrating the theoretical edge profiles thereof;

Figures 6(a), (b) and *(c)* are sections through another crystal device during various stages of manufacture;

Figure 7 is a fragmentary section to an enlarged scale, of another one of the crystal devices;

Figure 8 is a graph of Cos ϕ versus layer thickness for explaining the analysis of the crystal device of Figure 7;

Figures 9(a) and *(b)* are fragmentary sections through yet another one of the crystal devices during different stages of manufacture;

Figures 10(a) and *(b)* show scanning electron microscopic photographs of selectively etched cleavage faces of the crystal device of Figure 9;

Figures 11, 12 and *13* are fragmentary sections through three further ones of the crystal devices; and

Figures 14(a) and *(b)* are fragmentary sections through a further one of the crystal devices at different stages of manufacture thereof.

In the methods of epitaxially growing crystal devices to be described, molecules are transported in one direction and in an environment of such reduced pressure that the mean free path ℓ of the molecules is substantially longer than a source-to-substrate distance L.

The apparatus shown in Figure 1 is arranged to carry out a molecular beam expitaxial growth process. A substrate holder 12 whose temperature is controlled by means (not shown) is rotatable through angles of ± 180° about an axis Z extending normal to the plane of its surface. A GaAs substrate 13 prepared in a manner to be described in more detail hereinafter is placed on the holder 12 with a layer of liquefied metal sandwiched between itself and the holder 12. A plurality of spacially separated beam sources 14 to 21 are provided. Each beam source is made of high-purity, heat-resisting material and contains a high purity source material. Each beam source has its own temperature control unit and each is arranged to emit a beam of molecules to the major surface of the substrate 13. The intensity of the beam is proportional to the vapour pressure of the material contained in the source. Each of the beam sources 14 to 21 has a circular aperture 6 mm in diameter and is spaced from the substrate by a distance L = 8 cm. The beam sources 14 and 16 respectively containing source materials Ga and Aℓ are disposed in the x-z plane while the beam sources 15 and 17 both having As as source material are located in the y-z plane. The axis of each of the beam sources 14, 15, 16 and 17 is inclined at 25° relative to the z-axis. The beam source 18 lies on the z-axis, the axes of the beam source 19 and 20 lie in the x-z plane, and the axis of the beam source 21, lie in the y-z plane. The axes of each of the beam sources 19, 20 and 21 is inclined at an angle of 35° relative to the z-axis. The positions of the beam sources 14 to 21 are interchangeable, and these beam sources can be arranged to supply any combination of source materials. Except for the As beam source 17, the remaining beam sources are provided with shutters (not shown) actuable independently of each other. The substrate holder 12, the substrate 13 placed thereon, the beam sources 14 to 21 and their shutters are all housed in an ultra-high vacuum container which is evacuated to a pressure less than 5 x 10^{10} torr.

Figure 2 shows a (100) GaAs substrate 12 masked with a photoresist mask 22 and etched with a conventional preferential etchant ($H_2SO_4 : H_2O_2 : H_2O = 1 : 8 : 1$), to form recesses or grooves having different cross-sectional configuration due to the undercuts formed. The difference in the undercut of each groove depends partially upon the direction in which the grooves extend in the photoresist mask 22 as best shown in Figure 6(a). The cross-sectional configurations of these recesses or grooves also depend upon the crystal faces which are presented for etching as shown in Figures 2(b), (c) and (d).

Example 1

An Si-doped, n-type GaAs substrate block 13 of 1 x 1 cm square was prepared so as to have a mirror-polished (100) major surface with four sides consisting of the (110) cleavage faces. The substrate was masked with photoresist strips of about 10 microns in width and oriented in the $<0\overline{11}>$ direction within a tolerance of less than 30″, and then etched to about 5 microns in depth with the etchant described above. After the photo-resist mask had been removed, the whole major surface was etched with the same etchant for about five seconds, washed and dried. The result was the provision of a three dimensional configuration of predetermined geometry in one major face of the crystal substrate. Immediately thereafter, the substrate 13 was placed on the holder 12 in such a manner that the direction $<0\overline{11}>$ of the substrate 13 extended parallel to the x-axis (see Figure 1).

The vacuum container was then evacuated to a pressure of less than 5 x 10^{-10} torr, and thereafter the As beam source 17 was heated to emit As_4 molecules directed at the major surface of the substrate 13 (etched as shown in Figure 2) while the substrate 13 was maintained at a temperature of 610°C for ten minutes. Thermal etching was thereby effected. Thereafter the substrate 13 was maintained at a temperature of 550°C, and the shutter of the Ga beam source 14 which source had been preheated was opened to allow a beam of Ga_4 molecules to impinge upon the substrate 13 while the Ga beam 23 from the Ga beam source and the As_4 beam 24 from the corresponding beam source were directed at the substrate so that GaAs crystals were grown to a depth of 0.84 microns.

Figure 3 is a $(0\overline{11})$ section through an expitaxially grown layer of a structure 25, the beam directions being indicated by the arrows. As described above, the direction $<01\overline{1}>$ of the substrate extended parallel to the x-axis so that in the y-z section, that is, in the $<01\overline{1}>$

plane, the As_4 beam 24 is incident on the substrate at an angle of 25° to the perpendicular to the substrate from the upper right hand side (as viewed in Figure 5) while the incidence angle of the Ga beam 23 is perpendicular to the substrate. As a result, the As_4 beam 24 will impinge upon the top surface 26 of the structure 25 and on its right hand side surface, but the As_4 beam 24 will not directly impinge upon a portion 28 of the under-surface 27*a* located immediately at the left hand side of the structure. The Ga beam 23 is uniformly incident on the regions 27*a* and 27*a* which are not shadowed by the structure 25 and on the top 26 of the structure 25.

In a molecular beam epitaxial process using GaAs beams on a flat substrate, the sticking coefficient of Ga is almost unity, and of the incident As_4 molecules only those which react with Ga adhere to the substrate while any remaining As_4 molecules are scattered away from the substrate. Therefore when the As_4 beam 24 is of higher intensity than the Ga beam 23, GaAs crystals will stoichiometrically grow in proportion to the local arrival rates of the Ga beam and not the As_4 beam. Where crystal growth continues for a long tme with an insufficient supply of As_4 molecules, Ga liquid drops form on the surface. However, the region on which the As_4 beam 24 impinges directly is supplied with excess As_4 molecules. This was confirmed by the illumination of the crystal growing surface with a diffraction electron beam in the x-axis direction in Figure 1.

When the molecular beam epitaxy is continued under the above conditions, crystal layers 29*a*, 29*b* and 30 are grown. The molecular epitaxial growth will be described in more detail with further reference to Figure 4. In Figure 4, the left hand edge portion 31 of the layer 29*b* is indicated by black dots (·). In order to make a theoretical analysis of the configuration of the edge 31, it is assumed that (I) the Ga beam is uniformly emitted through the aperture over an area S of the Ga beam source; and (II) the presence of excess As in the surface diffusion length of Ga adhered to the surface of grown crystal layer is negligible.

Referring now to Figure 5, the arrival rate of Ga molecules from the Ga beam source at a point (ys, t) is in proportion to an area Sy of the aperture of the Ga beam source when viewed from the point (ys, t), the line of sight being restricted by the upper edge of the inverted-mesa shaped structure 25. The equation:

$$Sy = \int_{r}^{R+R_o} \sqrt{R^2 + (Y-R_o)^2}\, dy$$

can de deduced where

$Y = [L\ (d \tan \theta + g - ys)\ t\ (d \tan \theta + g) + ys\ dg]\ /(dg - t)$

$R_o = L \tan \theta$

$dg = d + h$, and

θ = the incidence angle of the Ga beam.

The epitaxial layer 30 grows as fast as the layer 29*b* so that the former expands outwardly, forming an overhang g.

$$g = H \tan \beta = h_f\ to \tan \beta/tof$$

β is called the inverted mesa angle and is 22.5°. When the growth of the overhang *g* is taken into consideration in the theoretical calculation of the profile of the edge portion 31, the curve B is obtained as shown in Figure 4. The curve A indicates the edge profile when the growth of the overhang *g* is not taken into consideration. The real edge profile indicated by the black dots is similar to the theoretical curve B with very small errors of the order of ± 200Å. From this it can be concluded that the assumption (I) was correct.

In Figure 4, the profile of the right hand side edge portion 32 of the layer 29 (see Figure 3) is also indicated by small black triangles (Δ). The curve has a gentle slope. It is assumed that individual Ga atoms diffuse into the surface of the substrate and that the lifetime of each Ga atom prior to its combination with As is *r*. Based on this assumption the profile of the edge 32 is theoretically expressed by the equation

$$\exp\ (-y/L_{Ga})$$

where $L_{Ga} = f\ (D_{Ga},\ r)$ and,

L_{Ga} and D_{Ga} are the diffusion length and the diffusion coefficient, respectively.

In Figure 4, the profile of the right hand edge of the layer 29*a* is semilogarithmically plotted with small black squares, and $L_{Ga} = 0.19 \pm 0.04$ microns is obtained from a straight line drawn along this curve. As described above, the region 28 (see Figure 3) is not bombarded with the primary As_4 beam so that the crystals grow under a Ga rich condition. Thus the effects of diffusion are sufficiently discernible.

From the above fundamental experiments or Example 1 it was deduced that (1) under an As rich condition, the diffusion length of Ga is extremely short so that the local growth rate of the GaAs expitaxial layer is in proportion to the local arrival rate of Ga; (2) the surface diffusion length of Ga can be controlled by changing the arrival rate of As_4 so that it is possible to extend the epitaxial growth in a region not bombarded by Ga atoms; (3) a single crystal can be grown even under Ga rich condition without forming Ga liquid drops if a Ga rich region is localized.

Example 2

As shown in Figure 6, following the procedures of Example 1 as a semi-insulative GaAs substrate 34 having a (100) major surface was prepared, and by using the conventional methods and a p-type layer 35, 3 microns in thickness with a hole concentration of about 5 x 10^{14} cm^{-3} was formed on the substrate 34. An n-type layer 36 was formed over the p-type layer 35 to a depth of 0.5 micron with an electron concentration of about 5 x 10^{16} cm^{-3}. A p-type layer 37, 3 microns in thickness was formed over the n-type layer 36 with the concentration of holes of 1 x 10^{18} cm^{-3}. Following the procedures of Example 1 the p-type layer 37 was etched to expose the n-type layer (see Figure 6*b*). Thus prepared substrate 34 was placed on the holder (see Figure 1) in a manner substantially similar to that described in Example 1, and thereafter the As beam sources 15 and 17 were heated to emit sufficient As_4 molecules in the beams 39 and 40 onto the heated substrate for effecting thermal etching. Thereafter, the shutters of the Ga beam source 14 and the Ge beam source 16, which had been preheated, were opened to cause the Ga 41 and Ge 42 beams to impinge upon the substrate to grow n^+ epitaxial layers 43*a*, 43*b*, 44*a*, 44*b* and 44*c*, each having a thickness of one micron and being doped with 1 x 10^{18} cm^{-3} of Ge. Since the As_4 beams impinge from both right and left hand sides of inverted-mesa shaped structures 38*a*, 28*b* and 38*c*, the epitaxial layers are symmetrically grown on both sides of each structure and are free from an abnormal growth on one side of the structure 38.

Example 3

Example 3 is aimed at illustrating that the local GaAs epitaxial growth rate is in fact proportional to the local arrival rate of Ga. Following the procedures of Example 1, a mesa type structure was formed as shown in Figure 2(d), and after the photoresist had been stripped off, the substrate was placed on the substrate holder with the <011> mesa direction extending parallel to the y-axis. The substrate was maintained at a temperature of 600°C, and the GaAs epitaxial growth was effected using only the Ga beam source 14 and As beam sources 15 and 17. In order to eliminate the Ga diffusion effects, an As rich condition was maintained during the whole epitaxial growth period. After cleavage along its (011) face, the substrate was subjected to stain etching so that the boundary between an epitaxial layer 46 and the substrate 13 could be clearly seen (see Figure 7). As shown in Figure 7 the Ga and As_4 beams 47 and 48 are respectively indicated by the solid-line arrows and the broken-line arrows, respectively.

Thicknesses Dv and Dp at arbitrarily selected points on the epitaxial layer 46 are plotted in Figure 8; the thickness Dv being measured in a direction perpendicular to the major surface of the substrate 13 while the thickness Dp being measured in a direction extending parallel to the incidence direction of the Ga beam. The angle ϕ is the angle between the direction of incident Ga beam and the vertical to the major surface of the substrate 13. From Figure 8 it will be appreciated that the depth Dv is proportional to cos ϕ while the depth Dp is the same at various points. This means that the GaAs crystal growth is in proportion to the local arrival rates of Ga beam which in turn are dependent upon the profile of the mesa structure and the incidence angles of the Ga beam. In addition, because the thickness Dp is the same throughout the epitaxial layer 46 this means that in a projection plane there exists a projected line (extending in the direction of the Ga beam) which indicates that the concentration of Ga per unit area is constant.

Example 4

It is well established that in molecular beam eptiaxity using semiconductors in Groups III and V of the Periodic Table, the sticking coefficient of atoms in the Group III is almost equal to unity. Therefore the results obtained in Example 3 may be applied to the growth of mixed crystals of atoms in the Group III such as $Ga_{1-x}A\ell_xAs$ in order to epitaxially grow three-dimensional structures.

Following the procedures of Example 3, a pattern of photoresist strips with a pitch of 8 microns in parallel with <011> direction and oriented in the <0$\bar{1}$1> direction are formed upon the (100) major surface of a GaAs substrate. Thereafter, followng the procedures of Example 1, the substrate was subjected to etching. Figure 9 shows a (011) section through the thus treated substrate 49 which as can be seen has valleys and ridges. The substrate was placed on the substrate holder with the <011> direction extending parallel to the y-axis (see Figure 1). The As beam sources 15 and 17, the Ga beam source 14 and the Aℓ beam source 16 were used to effect the epitaxial growth of a multilayer of GaAs-$Ga_{1-x}A\ell_xAs$. During the epitaxial growth, the shutters of the Ga beam source 14 and the As beam sources 15 and 17 were kept opened while the shutter of the Aℓ beam source was intermittently opened and closed in order to epitaxially grow a multilayer consisting of GaAs layers alternating with $Ga_{1-x}A\ell_xAs$ layers.

Figure 9(b) shows diagrammatically a (011) section through the substrate or specimen after five layers had been formed; the Ga, Aℓ and As_4 beams being indicated by respective arrows 55, 56 and 57. While the layers 50, 51 and 54 were being grown, the shutter of the Aℓ beam source 16 was kept closed so that these layers 50, 51 and 54 are GaAs layers. While the layers 51 and 53 were being grown, the shutter of the Aℓ beam source 16 was kept opened so that these two layers are $Ga_{1-x}A\ell_xAs$ layers. Hot phosphoric acid is an etchant which cannot attach to the GaAs layers but attacks the $Ga_{1-x}A\ell_xAs$ layers at a high etching rate which is increased as the concentration of Aℓ (x) is increased. The cross-hatched area in Figure 9(b) is a region where the Aℓ concentration is high.

Figure 10 shows scanning type electron microscope photographs of the (011) cleavage face of a specimen which had been immersed in hot phosphoric acid at 100° for three minutes in order to selectively etch the high A concentration regions in $Ga_{1-x}A\ell_xAs$ layers. Figure 10 (a) is a photograph of the same view at a low magnification showing valleys with a pitch of 8 microns in length between one ridge and the next one. Dark areas correspond to the regions with a high Aℓ concentration. Because of the selective or preferential etching the etched regions are in the form of cavities which correspond to the cross-hatched areas in the layers 51 and 53 shown in Figure 9(b). The photograph of Figure 10(b) shows to an enlarged scale a local area of a multilayer film formed on valleys and ridges with a pitch of 16 microns. It is seen that etched depth changes smoothly, which indicates that the composition x in the $Ga_{1-x}A\ell_xAs$ layer is varied smoothly depending upon the arrival rates of Ga and Aℓ beams.

While the dependence of the Aℓ concentration x has not been investigated in detail, it is observed that the concentration distribution as well as the film thickness can be readily analyzed based not only on the fact that the sticking coefficients of Ga and Aℓ are substantially equal to unity but also the results obtained from Examples 1 and 3. Referring back to Figure 9(b), a vertical line n is erected at a point p arbitrarily selected in the interface between the $Ga_{1-x}A\ell_xAs$ layer 51 and the GaAs layer 50 below. Angles between the vertical line n and the directions of incident Ga and A beams 56 and 57 are respectively designated ϕ_{Ga} and ϕ_A, and the arrival rates of Ga and Aℓ beams with $\phi_{Ga} = 0$ and $\phi_A = 0$ are respectively denoted by I_{Ga} and I_A. Then the concentration Xp and the thickness of the layer 51 at the point p are given by the equation:

$$Xp = \frac{I_A \cdot \cos \phi_A}{I_{Ga}.\cos \phi_{Ga} + I_A .\cos \phi_A}$$

$$D_O = C. (I_{Ga}.\cos \phi_{Ga} + I_A .\cos \phi_A)$$

where C = a constant of proportionality.

In like manner, the concentration Xp and the thickness D_O can be obtained at various points because the profile of the mesa shaped structure as well as the directions of incidence of beams are known. The characteristics of the depth D_O are clearly indicated by the thickness of the cavities in the $Ga_{1-x}A\ell_xAs$ layers which were selectively etched as shown in Figures 10(a) and 10(b) and by the variation in thickness of the GaAs layer remaining between these cavities. In addition the variation in depth of the cavities shown in Figure 10(b) clearly and qualitatively indicates the dependence of the concentration X on beam position.

Example 5

Following the procedure of Example 4, the epitaxial growth of a multilayer consisting of $Ga_{1-x}A\ell_xAs$ and GaAs layers was effected. A substrate was placed on the substrate holder with the <011> direction extending parallel to x-axis (see Figure 1). Using the Ga beam source 14 and the As beam sources 15 and 17, a GaAs layer was grown first. Thereafter, the shutter of the Aℓ beam source which had been preheated was opened to allow the growth of an $Ga_{a-x}A\ell_xAs$ layer. Then the substrate holder was rotated through 90° so that the

<011> direction of the substrate extended in parallel to the y-axis (see Figure 1), and thereafter layer of $Ga_{1-x}A\ell_xAs$ was grown. After the $Ga_{1-x}A\ell_xAs$ layer had been grown to a predetermined thickness, the substrate holder was rotated through 180° so that the direction <011> was parallel with the -y direction and a further layer was then grown. These steps were cyclically repeated to form a multilayer of $Ga_{1-x}A\ell_xAs$. Thereafter the direction <011> of the substrate was brought into parallel relationship with the x-axis again, and yet another layer of $Ga_{1-x}A\ell_xAs$ was grown. Finally the shutter of the $A\ell$ beam source was closed so that the last layer was a GaAs layer. During the epitaxial growth, all of the beam sources were so controlled that an As rich condition was maintained. The specimen was cut along (011) and was subjected to etching so that the structure of the multilayer could be clearly seen. The specimen was further subjected to selective etching with hot phosphoric acid so that cavities were observed as shown in Figure 10. This shows that the arrival rates of $A\ell$ and Ga beams varied depending upon the orientation of the substrate.

Example 5 illustrates that the arrival rates of beams of molecules at an arbitrarily selected point on a crystal growth surface can be varied by changing the relative position of the substrate with respect to the beam sources.

Example 6

Following the procedures of Example 4, a substrate was prepared and placed on the substrate holder with the <011> direction oriented so as to extend parallel with the x-axis. The chemical GaP was loaded into the beam source 15 (see Figure 1), and together with the Ga beam source 15 (see Figure 1), and together with the Ga beam source 14 and the As beam source 17 was used to effect epitaxial growth. Figure 11 shows schematically a (011) section through the substrate and indicates the directions of incident beams 62, 63, 64 and 65. The beams 62 and 63 are respectively a Ga beam from the Ga beam source 14 and a GaP beam from the GaP beam source 15. The beam 64 is a P_2 beam from the GaP source, and the beam 65 an As_4 beam from the As_4 beam source 17. The shutter of the GaP source 15 was kept closed while a layer 60 was grown. After three layers 59, 60 and 61 had been grown, the specimen was cut along the face (011) and was subjected to etching with an A-B etchant at room temperature. This etchant etches GaAs at a high rate, but the etching rate decreases as the concentration *y* of P in the compound $GaAs_{1-y}F_y$ increases. It was observed on the etched face through a scanning type electron microscope that the regions of high P concentrations (cross-hatched area in Figure 11) were left unetched.

In contrast to the mixed crystals of atoms in Group III such as $Ga_{1-x}A\ell_xAs$ described in Examples 4 and 5, the concentration y of a mixed crystal $GaAs_{1-y}P_y$ including the atoms of Group V, cannot be simply determined by the arrival rates of As_4 and P_2 beams, but experimental results show that the region at which the arrival rate of P_2 beam is high has a higher concentration y.

So far the selective epitaxial growth of GaAs and its mixed crystals has been described. As described in Example 1, the surface diffusion length of Ga can be made shorter than 200Å. The surface diffusion length varies depending upon the conditions set up during crystal growth. In so far as the diffusion length can be made smaller than the size of self-masking it is possible to selectively grow crystals having a composition depending upon the local arrival rates of molecular beams.

Since the behaviours of impurities on the surface of grown crystal layer are different from one impurity to another, the following precautions must be taken when doping impurities into crystals:

(a) Impurities having a sticking coefficient substantially equal to unit are Si and Sn which are donors, Mn and Be are acceptors and Ge which is an ampho ion. These donors and acceptors can be doped selectively by the above described methods, and the concentrations of dopants will be determined as a function of local arrival rates of dopant beams as described in detail in Example 4. However, with impurities such as Sn which has a high segregation coefficient and tends to move considerably during crystal growth of for example GaAs, the doping profile tends to become large. When the distance that the impurity can move is short compared with the size of multilayer structures, the movement of the impurity will be negligible.

Ge, which is an ampho ion, acts as a donor under As rich conditions and as an acceptor under Ga rich conditions. When GaAs is grown on a flat surface under a Ga rich condition, using the method described in detail in Example 1, no Ga liquid droplets will be formed even under a Ga rich condition so long as the Ga rich region remains smaller. Therefore it follows that when the profile of a structure is so selected that locally Ga and As rich regions are formed and Ge is doped, Ge serves as a donor in the As rich region while serving as an acceptor in the Ga rich region.

(b) Mg is an acceptor whose sticking coefficient is greatly dependent upon the composition of crystals. For example, the sticking coefficient of Mg to $Ga_{1-x}A\ell_xAs$ is about 1×10^{-5} when $x = 0$, and about 7×10^{-3} when $x = 0.2$. Therefore even when the angle of the incident beam of Mg molecules is not strictly controlled, Mg is automatically selectively doped into high A concentration regions.

Next some Examples of doping will be described.

Example 7

Referring back to Figure 1, beam sources 15 and 17 were loaded with As and beam source 18 loaded with a p-type dopant or Mg. The beam source 19 was loaded with an n-type dopant or Sn in the x-z plane and inclined at an angle of 35° relative to z-axis. The temperatures of these beam sources 15, 17, 18 and 19 were so determined that an epitaxial layer of $Ga_{1-x}A\ell_xAs$ grown on a flat substrate produced a doped layer in which $x = 0.1$. An As rich condition was maintained during epitaxial growth, and an Sn concentration of $3 \times 10^{18}/cm^3$ was obtained when the Sn beam source 19 was energized. The hole concentration of $1 \times 10^{18}/cm^3$ was attained when the Mg beam source 18 was energised.

Following the procedures of Example 4, the substrate was formed with alternate ridges and valleys with a pitch of 200 microns, and placed on the substrate holder with the (011) direction oriented to extend parallel to the x-axis. Using the Ga beam source 14, the As beam sources 15 and 17 and the Sn beam source 19 a first n-type GaAs buffer layer was grown. Thereafter the substrate was rotated so that the <011> direction extended parallel to the y-axis, and the shutters of the Aℓ beam source which had been preheated to a predetermined temperature, and of the Mg beam source 18 which had been preheated to a temperature of 300°C were opened while the Mg beam source 18 was immediately heated to a predetermined Mg beam emission temperature. A $Ga_{1-x}A\ell_xAs$ layer doped with Sn and Mg was then grown to a predetermined thickness. The thus obtained specimen was subjected to heat-treatment in an As atmosphere, and cut along the (011) face. Figure 12 schematically shows a (011) section of the specimen. The layer 67 formed on a structure 66 is a Sn-doped GaAs layer, and the layer 68 is an Sn- and Mg-doped $Ga_{1-x}A\ell_xAs$ layer. The arrows indicate the direction of incident beams during the growth of the layer 68, and 71, 72, 73 and 74 are respectively indicative of the directions of the Ga, Aℓ, Mg and Sn beams (the As_4 beam not being shown).

Tests for conductivity and observations of the stain etched and selectively etched cleavage faces gave the following results:

a) the region 69 in the layer 68 had a high Aℓ concentration and was p-type;
b) the region 70 had an especially low Aℓ concentration and was n-type; and
c) the remaining region was of n-type.

These findings indicate:

(I) the variation in Aℓ concentration is similar to that described in Example 4;
(II) only the region 69 had a high Aℓ concentration and was of p-type, this probably being due to the dependence of sticking coefficient S of Mg on the composition of $Ga_{1-x}A\ell_xAs$. That is, when $x = 0$, $S = 10^{-5}$, but when $X = 0.2$, the sticking coefficient S suddenly increases to a level of 7×10^{-3}; and
(III) the remaining region was of n-type, this probably being due to the distribution of local arrival rates of the Sn beam and the decrease in sticking coefficient of Mg accompanied by the relative decrease in Aℓ concentration.

Example 8

The beam sources 18 and 19 were respectively loaded with Ga and Sn while the beam source 20 was loaded with Zn and located in the x-z plane inclined at an angle 35° relative to the z-axis. Following the procedures of Example 7, an n-type GaAs substrate with a (011) major surface was formed with alternate ridges and valleys having a pitch of 200 microns. This substrate was placed on the substrate holder with the direction <011> oriented to extend parallel to the y-axis. With the As beam sources 15 and 17, the Ga beam source 18, the Sn beam source 18 and the Zn beam source 20, an Sn- and Zn-doped GaAs layer was grown. The temperatures of these beam sources were so controlled that the doping concentrations of Sn and Zn in the GaAs epitaxial layer grown on the (100) major surface of the GaAs substrate were $3 \times 10^{18}/cm^3$ and $1 \times 10^{18}/cm^3$, respectively. The acceleration voltage of Zn^+ ions was 1,000V.

Figure 13 illustrates the (011) cross-section of thus obtained specimen, and arrows 78, 79, 80 and 81 indicate the direction of the Ga, As_4, Zn^+ and Sn beams. Following the procedures of Example 7, it was found that a region 77 in an epitaxial layer 76 formed on a structure 75 was of p-type while the remainder was of n-type.

Example 9

The beam sources 15 and 17 were loaded with As_4 while the beam sources 18, 16, 19 and 20 were respectively loaded with Ga, $A\ell$, Si and Mn. A photoresist Az-1350J was applied to the (100) major surface of a Si-doped, n-type GaAs substrate, and holography with an Ar ion laser was employed to project an interference fringe pattern with parallel fringes spaced by 3,700Å and oriented to lie parallel to the <011> direction of the substrate within a tolerance of ± 1′. Thereafter the substrate was etched with the etchant described in Example 1 so that ridges and valleys were left on the (011) major surface of the substrate 82 was illustrated in Figure 14(a). The substrate 82 was placed on the substrate holder with the <011> direction oriented to lie parallel to the y-axis (see Figure 1). Following the procedure of Example 1, a $Ga_{1-x}A\ell_xAs$ layer 83 selectively doped with Si and Mn was grown to a thickness of about 0.2 um, and thereafter a $Ga_{1-x}A\ell_xAs$ layer 86 was grown and doped with Si only. The total thickness of the two layers 83 and 86 was about 1.5 um. During the epitaxial growth process, the ratio of intensity between the Ga and $A\ell$ beams was maintained at 3:1 while the intensities of the Si and Mn beams were so controlled that their concentrations were respectively $2 \times 10^{18}/cm^3$ and $1 \times 10^{18}/cm^3$.

Figure 14b schematically depicts the structure of the epitaxial layer, and the arrows 87, 88, 89 and 90 indicate the direction of the incident Ga, $A\ell$, Si and Mn beams (the As beams are not shown). Observations through a scanning type electron microscope of the (011) cleavage face which was subjected to selective and stain etchings revealed the following:

(I) The $A\ell$ concentration was higher in a region 84 than in a region 85;

(II) As the average thickness D_{av} of the epitaxial layer approaches the pitch or spacing (3,700Å) of the ridges and valleys on the substrate, the surface roughness of the epitaxial layer became smoother and the variation in $A\ell$ concentration decreased;

(III) When the average thickness of the epitaxial layers 83 and 86 is increased relative to the pitch or spacing of the ridges and valleys of the substrate, the surface of the layer 86 became smoother and the $A\ell$ concentration in the $Ga_{1-x}A\ell_xAs$ layer was more uniform; and

(IV) The measurement of the conductivity in regions 84 and 85 was extremely difficult because these regions were extremely small. The donor impurity Si used in this Example was found to exhibit a low segregation effect and so it was assumed that the concentration in these small regions is also dependent upon the variation in local arrival rate of the beams.

As described above, the methods used in the described examples produced an epitaxial layer having a fine and three-dimensional structure and are thus suitable for improving the quality of various semiconductor devices and for fabricating novel semiconductor devices.

The methods described are generally based on the following observed facts:

(I) Epitaxial molecular beams travel along straight paths;

(II) The local arrival rate of a uniformly emitted epitaxial molecular beam can be varied by forming a structure having a suitable geometrical configuration upon a substrate; and

(III) The surface diffusion length of an atom or molecule stuck to the surface of a grown crystal layer can be controlled and can be made extremely short (less than 200Å) by suitably controlling the conditions of the molecular beam epitaxial growth process.

So far the methods have been directed to semiconductors in Groups III and V such as GaAs, $Ga_{1-x}A\ell_xAs$ and $GaAs_{1-y}P_y$, but it will be appreciated that the described methods can be applied to epitaxially growing crystals of semiconductors in other Groups and Non-semiconductors such as dielectric and magnetic substances. Furthermore, the methods are not limited to molecular beam epitaxy in a narrow sense, but can be applied to any crystal growing application which may satisfy the condition that the mean free path (l) of molecules is greater than a source-to-substrate distance (L).

Examples 1 to 9 disclose crystals having novel structures, and some modifications of the crystal growing methods. Some applications for semiconductor devices and novel semiconductors which are now feasible by the described methods will now be described.

(I) Those pertaining to Example 1:

(a) Applications: Formation of separated layers, self-aligning or registering, and selective epitaxial growth.

(b) Modifications: An etching mask of SiO_2 or Si_3N_4 is left unstripped after etching, and an epitaxial layer is grown on the remanent etching mask so that the selective epitaxy utilizing undercuts left after etching can be effected.

(c) Novel semiconductors devices: Example 1 discloses a fundamental crystal growing method so that various semiconductor devices could be devised. The self-alignment or registration attainable by the described method could be widely used in application such as in the fabrication of field-effect transistors (see Figure 6).

(II) Those pertaining to other Examples:

(a) Applications: Fabrication of various semiconductor and single crystal devices wherein the properties of a single crystal layer or film having a self-registering, three-dimensional structure are utilized.

(b) Modifications:

(b-1): Modifications of means forming on a single crystal substrate a three-dimensional structure having a geometrical configuration; for example a three-dimensional structure can have a multi-dimensional period. Instead of forming a three-dimensional structure by etching, it can be formed by selective epitaxial growth.

(b-2): Modifications of the angle of incidence of molecular beams and the relative positioning between a substrate and beam sources. The beam sources can be increased or decreased in number.

(c) Novel semiconductor devices: A multilayer device can be grown in a very simple manner so that a thin mixed crystal film having a multi-dimensional structure can be grown. Furthermore, a p- or n-type region can be selectively formed to provide application in (i) the fabrication of embedded hetero-optical transmission paths in semiconductor devices and (ii) the fabrication of light-emitting devices, optical moduclators, optical branching devices, and optical amplifiers as well as in the application of the hetero-optical transmission paths. The novel semiconductor device described in Example 8 and shown in Figure 14 is an aysmmetrical Bragg's reflector device, and when it is incorporated in a distribution-feedback type laser, both or either of the refraction index feedback or the emission feedback can be effected. Thus, the asymmetrical structure can be advantageously utilized. In addition, when this asymmetrical structure is used as a grating, further novel devices can be obtained.

WHAT WE CLAIM IS:-

1. A method of manufacturing a single crystal device comprising the steps of providing on one major surface of a crystal substrate a three-dimensional configuration of predetermined geometry, maintaining the substrate at a crystal growing temperature; directing at least one molecular beam from source means onto said substrate at an oblique angle relative to the major surface of said substrate and providing an environment between the source means and the substrate in which the mean free path of the molecules in the or each said molecular beam is greater than the distance between the molecular beam source means and said substrate, whereby to effect an epitaxially grown crystal layer in discrete local regions of said major surface of the substrate dependent upon the local arrival rates of said molecular beams at the major surface.

2. A method according to claim 1, wherein the grown of the layer is halted while the thickness of said epitaxial crystal layer in still smaller than the smallest peak to trough variation in said three-dimensional configuration.

3. A method according to claim 1, wherein the molecular beam source means is arranged to provide a molecular beam of a first Group element, the sticking coefficient of which to the substrate is unity and a molecular beam of a second Group element which only sticks to the surface of said substrate by reacting with said first Group element.

4. A method according to claim 3, wherein in a region of said substrate where the local arrival rate of the molecular beam of the first Group element is different to that of the remainder of the substrate, a local region of the crystal layer having a thickness proportional to the arrival rate is formed.

5. A method according to claim 3, wherein in one local region of the three-dimensional configuration in which the arrival rate of the molecular beam of said second Group element is lower than that of the molecular beam of said first Group element, the thickness of said crystal layer being thinner than that in another local region in which the arrival rate of the molecular beam of said first Group element is greater than that of the molecular beam of the second Group.

6. A method according to claim 3, wherein in the three-dimensional configuration the arrival rate of the molecular beam of said second Group elements is arranged to be lower than that of the molecular beam of said first Group elements in a selected region so that the thickness of the crystal layer in the neighbourhood of said area and where the molecular beam of the first Group of elements only impinges, is greater than that of said area.

7. A method according to any one of claims 3 to 6, wherein the source means provide a plurality of molecular beams of different elements of the first Group.

8. A method according to any one of claims 3 to 6, wherein the source means provides a plurality of molecular beams of elements of the second Group element.

9. A method according to any preceding claim, wherein the surface diffusion length of the molecules from at least one molecular beam which impinges upon the surface of the grown crystal layer is smaller than the peak to trough variation in the three-dimensional configuration.

10. A method according to any preceding claim, wherein said epitaxially grown crystal layer consists of a semiconductor compound consisting of atoms in Groups III and V of the periodic table.

11. A method according to claim 1, wherein the source means comprises a plurality of molecule supply sources which are selectively operable to direct means onto the substrate in accordance with the desired composition of the crystal to be grown, the sources being so oriented relative to the substate that depedent upon the angle of incidence of the molecular beams, in that configuration at each location discrete regions having different crystal compositions are formed due to the different local arrival rates of said molecular beams.

12. A method according to claim 11, wherein said epitaxially grown crystal layer consists of $Ga_{1-x}A1_xA_s$.

13. A method according to any preceding claim wherein the source means includes at least one supply source for emitting a beam of a desired impurity arranged to be discrete at regions where different types of local impurities or concentrations are required.

14. A method according to any preceding claim, including the step of varying the angle of incidence of said molecular beams by changing the orientation of said major surface relative to the molecular beams.

15. A single crystal device when manufactured by the method of any preceding claim.

16. A method of manufacturing a single crystal device the method comprising the steps of forming on one major surface of a crystal substrate a three-dimensional configuration of predetermined geometry, maintaining the substrate at a crystal growing temperature, directing at least one molecular beam from source means onto the substrate at an oblique angle relative to the major surface of said substrate, and providing an environment between the source means and the substrate in which the mean free path of said molecules in the or each said molecular beam is greater than the distance between the source means and said substrate, whereby to effect an epitaxially grown crystal layer in discrete local regions of said major surface of said crystal substrate separated from one another due to the variation in the local arrival rates of said molecular beams brought about by the predetermined geometry of the three dimensional configuration.

17. A method according to claim 16, including the step of varying the angle of incidence of said molecular beams by changing the relative orientation of said major surface and said molecular beam sources.

18. A method according to claim 16, wherein the peak to trough variation in the three dimensional configuration is made greater than the surface diffusion length of at least one type of material molecules arranged to impinge upon the surface of the grown crystal layer.

19. A method according to claim 16, wherein the provision of the three-dimensional configuration is effected by the selective etching of said crystal substrate.

20. A method according to any one of claims 16 to 19 wherein the epitaxially grown crystal layer consists of a semiconductor compound consisting of atoms in Groups III and V of the periodic table.

21. A method according to claim 20, wherein said epitaxially grown crystal layer consists of $Ga_{1-x}Al_xAs$ ($0 = x = 1$) or $GaAs_{1-y}P_y$ ($0 = y = 1$).

22. A method according to any one of claims 16 to 21, wherein the source means comprises a plurality of molecule supply sources which are selectively operable to direct beams into the substrate in accordance with a desired composition of the crystal to be grown, the sources being so oriented relative to the substrate so that dependent upon the angle of incidence of the molecular beams on the configuration at each location, discrete regions having different crystal compositions are formed due to the different local arrival rates of said molecular beams.

23. A method according to any one of claims 16 to 22, wherein the source means includes at least one supply source for emitting a beam of a desired impurity, arranged to be directed at regions where different types of local impurities or concentrations are required.

24. A method according to any one of claims 16 to 23, wherein said three-dimensional configuration is geometrically periodic.

25. A single crystal device manufactured according to the method of any one of claims 16 to 24.

26. A single crystal device substantially as hereinbefore described with reference to any one of Examples 1 to 9.

27. A method of manufacturing a single crystal device substantially as hereinbefore described with reference to any one of Examples 1 to 9.

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1589455 COMPLETE SPECIFICATION

8 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

FIG. 1

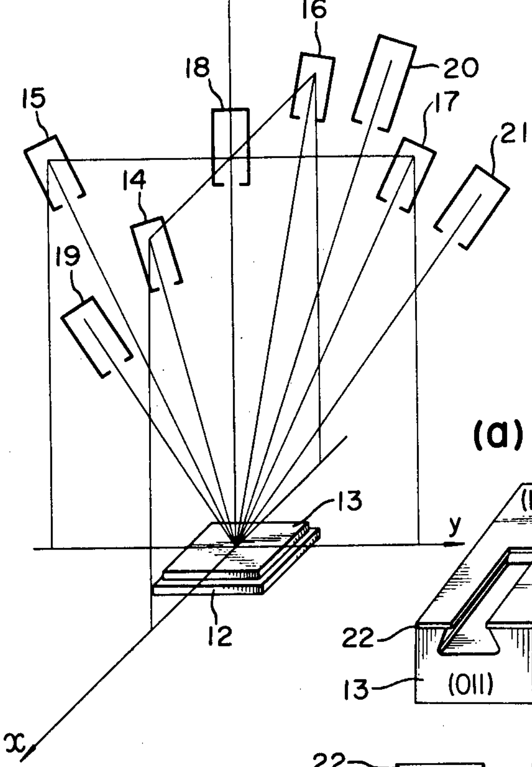


FIG. 2

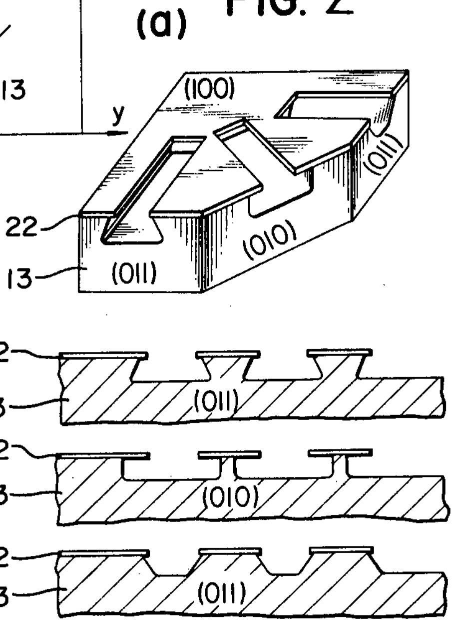
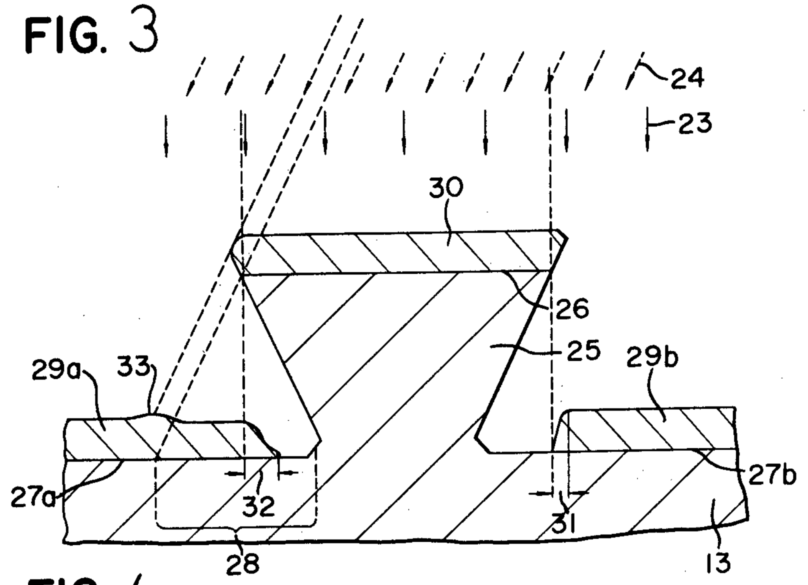


FIG. 3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29a
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29b
27b
27a
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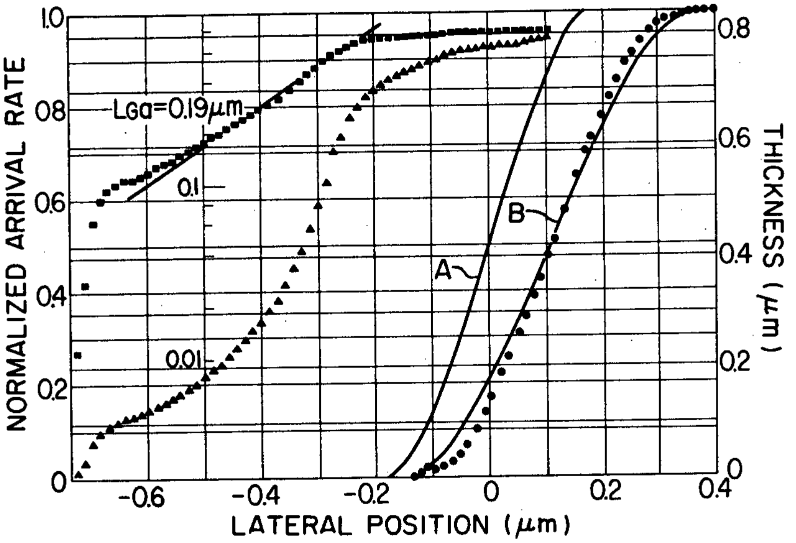
31
28
13

FIG. 4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0.8
0.6
0.4
0.2
0
Lga=0.19μm
0.1
0.01
A
B
THICKNESS (μm)
0.8
0.6
0.4
0.2
0
-0.6
-0.4
-0.2
0
0.2
0.4
LATERAL POSITION (μm)

FIG. 5

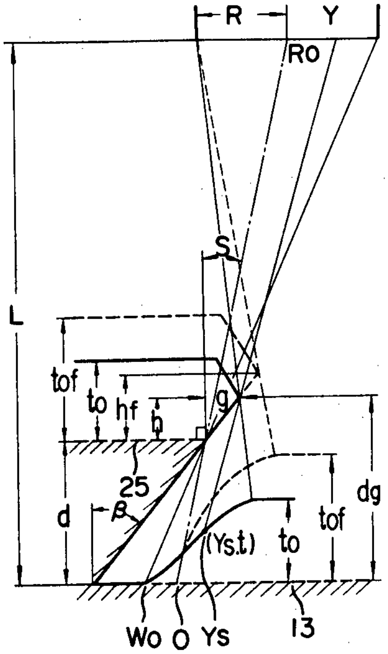

R
Y
Ro
S
L
tof
to
hf
h
g
25
d
β
(Ys.t)
to
tof
dg
Wo
O
Ys
13

FIG. 7

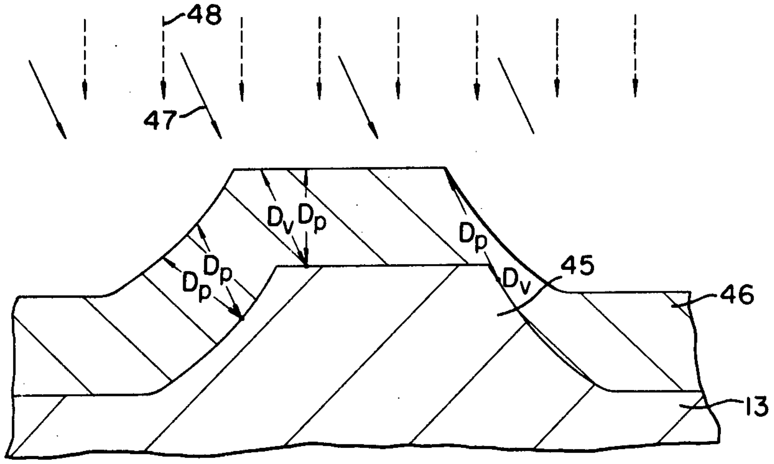

48
47
Dv
Dp
Dp
Dp
Dp
Dv
45
46
13

FIG. 6

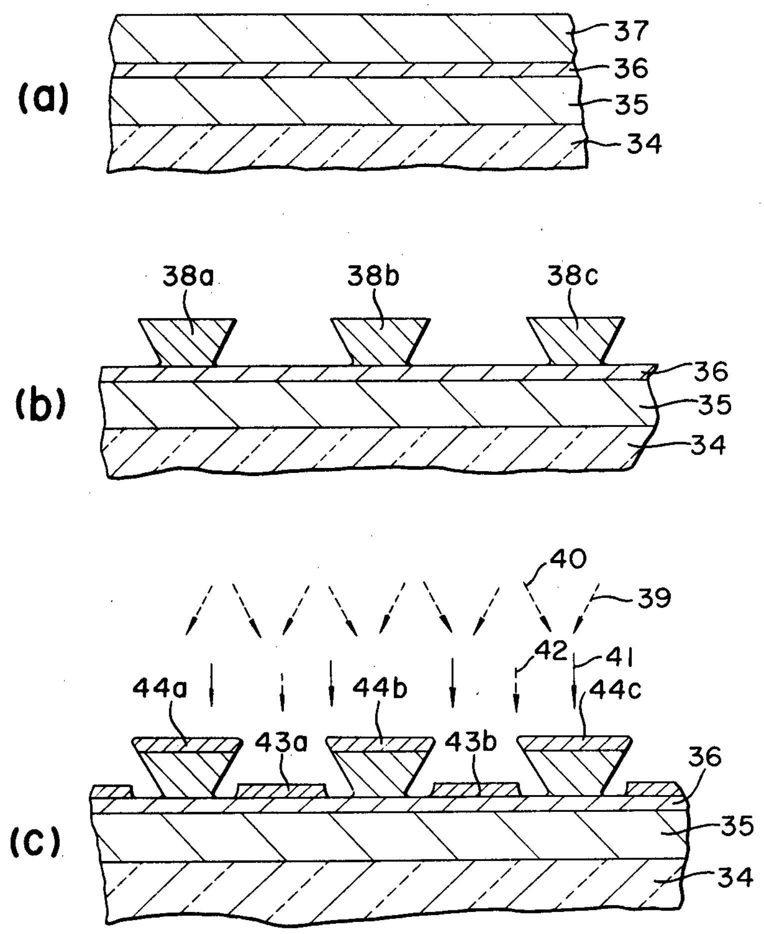

(a)
37
36
35
34
(b)
38a
38b
38c
36
35
34
(c)
40
39
42
41
44a
44b
44c
43a
43b
36
35
34

FIG. 8

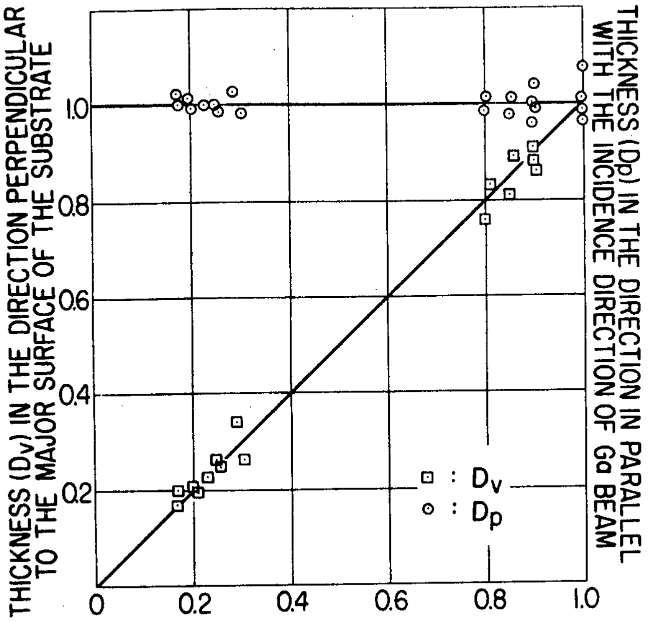

THICKNESS (Dv) IN THE DIRECTION PERPENDICULAR TO THE MAJOR SURFACE OF THE SUBSTRATE
THICKNESS (Dp) IN THE DIRECTION IN PARALLEL WITH THE INCIDENCE DIRECTION OF Ga BEAM
1.0
0.8
0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
1.0
□ : Dv
⊙ : Dp

FIG. 11

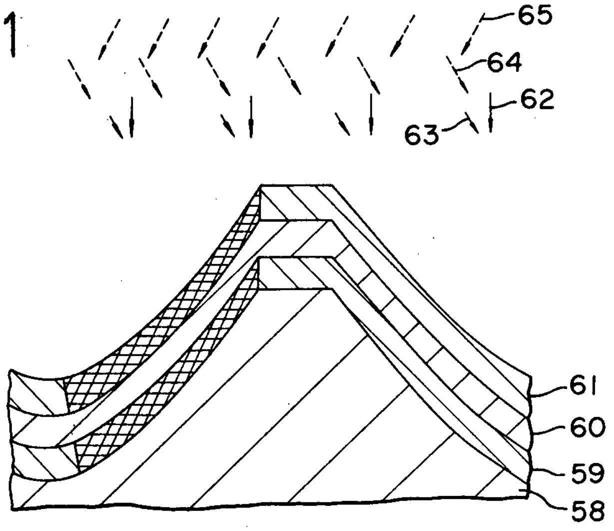
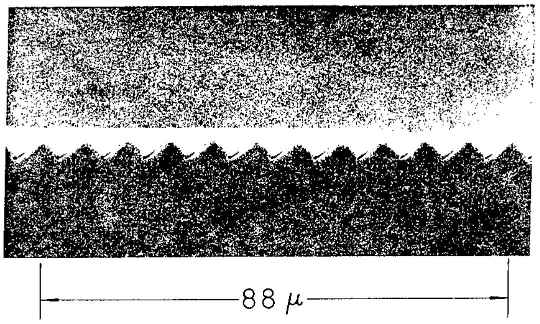

65
64
62
63
61
60
59
58

FIG. 10

(a)



(b)

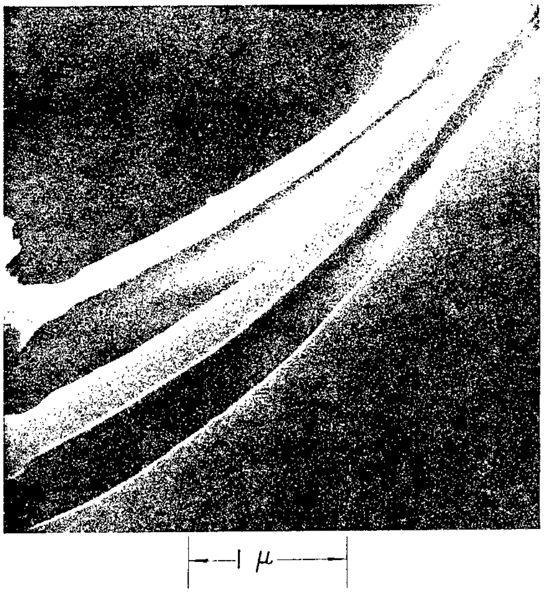


FIG. 12

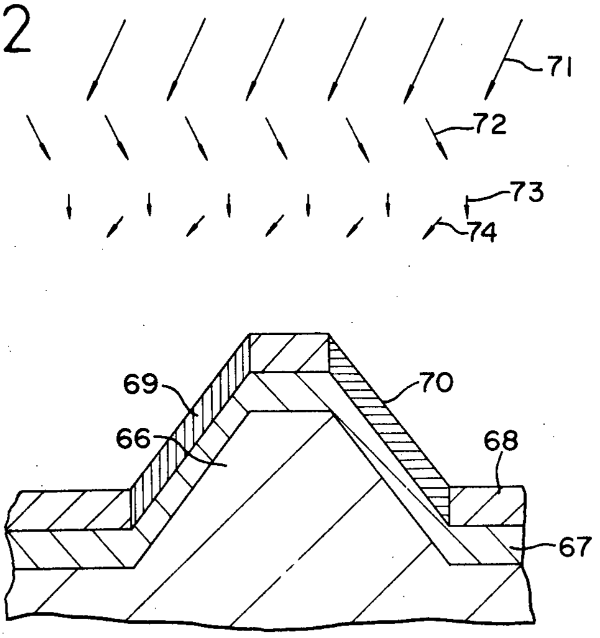


FIG. 13

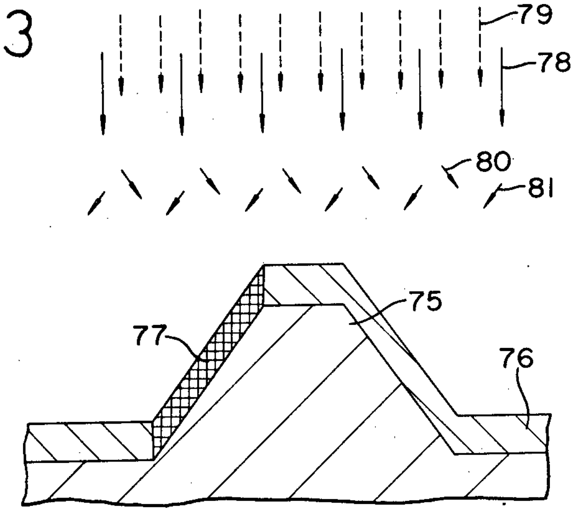


FIG. 9