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TREATMENT OF SEMICONDUCTIVE BODIES

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FIG. 1

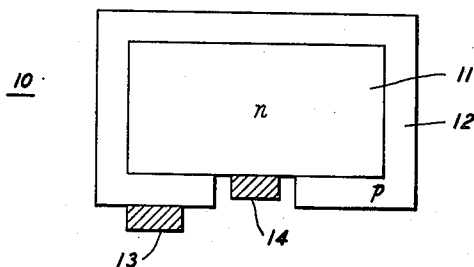


FIG. 2

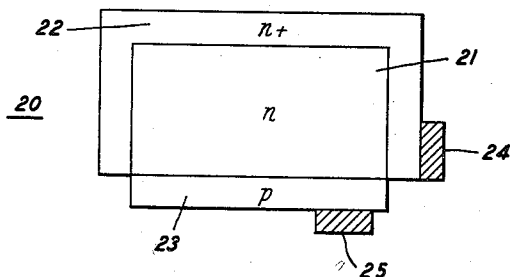
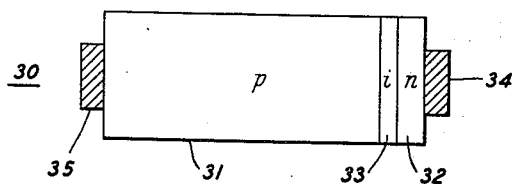


FIG. 3



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TREATMENT OF SEMICONDUCTIVE BODIES

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This invention relates to the fabrication of semiconductor devices, and more particularly to the preparation of semiconductor bodies for adapting them for use in semiconductor devices.

The semiconductors of greatest importance from the standpoint of device applications form predominantly covalent crystals, the atoms being held together by electron-pair bonds formed by the four valence electrons in a diamond-type lattice. A perfect crystal would be an insulator. To impart semiconductive properties to the crystal it is customary to add conductivity-type determining impurity atoms which take the place of semiconductor atoms in the crystal lattice. There are two main classes of conductivity-type determining impurities, donors and acceptors. The introduction of the former gives rise to free electrons in the crystal, the introduction of the latter to holes. In the fabrication of semiconductor bodies useful for device applications, it is necessary to distribute the conductivity-type determining impurities in a prescribed fashion for providing rectifying junctions within the bodies.

The present invention relates to improved techniques for providing a desired distribution of conductivity-type determining impurities in a semiconductor body.

Different conductivity-type determining impurities migrate or diffuse with varying rates and solubilities in a semiconductor crystal. Some which are introduced substitutionally in the lattice diffuse very slowly at temperatures much below the melting point of the semiconductor. The use of such impurities for achieving desired electrical properties in a semiconductor body has the disadvantage of requiring heating to high temperatures for effecting the desired distribution of such impurities. The use of high temperatures is undesirable because it increases the difficulty of manufacture and also usually results in degradation of the semiconductor. Other conductivity-type determining impurities which dissolve in a crystal more or less interstitially have diffusivities which are appreciable even at temperatures considerably below the melting point of the semiconductor. However, the use of such impurities hitherto has had the disadvantage that such impurities, being highly mobile, ordinarily tend to redistribute themselves with time throughout the body, upsetting the desired distribution. Because of this, it has been difficult to make reliable use of such impurities in the fabrication of devices. Accordingly, in spite of the disadvantages discussed, only those impurities which are introduced substitutionally have found any appreciable use.

One object of the present invention is to make feasible the use of conductivity-type determining impurities having high rates of diffusion for achieving desired electrical properties in a semiconductor crystal, thereby to facilitate the manufacture of various semiconductor devices. Typically, it is advantageous that the impurities have a diffusion rate in the range between 10^{-7} and 10^{-12} cm.²/sec. at the temperature employed for diffusion so that diffusion distance of practical interest may be realized in reasonable diffusion times, for example, diffusion times

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of no more than ten hours. To this end, the invention provides techniques for stabilizing in a semiconductive crystal conductivity-type determining impurities of the type which normally have the tendency to migrate even at temperatures considerably below the melting point of the semiconductor, such as at temperatures in the usual operating range of semiconductor devices.

The present invention is based to a considerable extent on the discovery of certain novel principles affecting the solubility and diffusion of conductivity-type determining impurities in a semiconductive crystal and on the correlation of such novel principles with known principles in the fabrication of semiconductive devices.

First, it has been discovered that the presence of a conductivity-type determining impurity of one type in a semiconductive crystal generally has a tendency to increase the solubility of a conductivity-type determining impurity of the opposite type and to increase the solubility of a conductivity-type determining impurity of the same type. In particular, in a semiconductive crystal containing a p-n rectifying junction, the solubility, for example, of an added donor which is capable of diffusing readily, tends to be higher on the p-type side than on the n-type side. Additionally, the electric field associated with a p-n junction acts to increase diffusion from the n-type side to the p-type side and to impede diffusion in the opposite direction. However, in the past such tendency had not been observed and so had not been exploited because the tendency was slight in those impurities which were being used most extensively since their rate of diffusion was too low at temperatures much below the melting point of the crystal. In accordance with the principles of the present invention, it is possible by appropriate choice of impurities to exploit this tendency.

It will be helpful to discuss many of the principles of the invention with specific reference to the use of lithium as the impurity in conjunction with either silicon or germanium as the semiconductor since lithium, which has donor properties in both germanium and silicon, diffuses readily therein at temperatures considerably below their melting points. However, it should become apparent that the principles of the invention have wider application.

Lithium has the further characteristic that it is readily depleted from a region underlying the surface of either a silicon or germanium crystal when the crystal is heated to a temperature at which the lithium migrates freely. In particular, it appears that the oxide layer which tends to form on silicon and germanium bodies acts as a sink for lithium. This characteristic in the past has severely restricted the usefulness of lithium as a conductivity-type determining impurity in either germanium or silicon.

As an exemplary application of the principles of the invention, the built-in electric field associated with a p-n rectifying junction is employed to prevent the lithium from reaching a surface where it will be withdrawn. In particular, by providing on either a germanium or silicon body a skin which is heavily doped with a donor element, there may be provided a built-in electric field near the surface which facilitates the introduction but inhibits the withdrawal of lithium from the interior of the body.

Additionally, it has been found in accordance with the invention that pairing of donor and acceptor ions in a semiconductive crystal may be employed advantageously to alter the solubilities and the rates of diffusion such impurities will have in the crystal. Ion pairing depends on the coulombic attraction of a pair of oppositely charged ions. For ion pairs to form in significant numbers, it is important that at least the ions of one charge be mobile in the crystal in the absence of ion pairing. Moreover, there is an increasing tendency for ion pairs which have formed to dissociate with increasing temperature. The extent to which the crystal temperature may be raised

without dissociation of the ion pair depends on the coulombic attraction between the two ions forming the pair. Most combinations of donors and acceptors will not produce a significant amount of stable ion pairing because at temperatures where the mobility of at least one group of ions is sufficiently high for ion pairing to occur, the thermal effects tending to cause dissociation exceed the coulombic attraction between the oppositely charged ions. Typically, it is advantageous that the binding energy of an ion pair be at least an electron volt.

Lithium, however, is typical of a conductivity-type determining impurity which does have a high mobility in silicon and germanium at temperatures sufficiently low that the coulombic attraction between its positively charged ion and the negatively charged ion of a suitable acceptor will withstand thermal dissociation. Accordingly, ion pairing may be employed to increase the solubility and decrease the diffusivity of lithium in silicon and germanium.

Ion pairing is found to exhibit certain phenomena. In particular, when an ion pair is formed the energy levels of both the donor and the acceptor are altered. The proximity of the negative acceptor ion to the positive donor ion decreases the difficulty of return to the donor state for an electron. Concurrently, the proximity of the positive donor ion to the negative acceptor ion increases the difficulty of return to the acceptor state for a hole.

Additionally, since ion pairs possess dipolar fields their presence provides scattering cross sections to the mobility of charge carriers very much smaller than that of point charges. This has important implications from a device standpoint.

In another aspect, the invention is based on useful applications of this ion pairing phenomenon.

In particular, use of ion pairing techniques may be employed advantageously in the compensation of an unbalance of conductivity-type determining impurities in a crystal. In the absence of ion pairing the addition of one conductivity-type determining impurity to a crystal to compensate for a conductivity-type determining impurity of opposite type has the concomitant effect of causing an undesirable decrease in the mobility of charge carriers in the crystal because of increased impurity scattering. However, in accordance with the invention by choosing the added impurity such that ion pairing results, an increase in the mobility of charge carriers may be made to accompany the decrease by compensation of the unbalance in the impurities in the crystal.

As previously indicated, it has been discovered that ion pairing is more pronounced with particular pairs of conductivity-type determining impurities than with others at a given temperature. In particular, it has been discovered that the ion pairing effect is enhanced and stability against thermal dissociation increased if at least one of the two ions involved is plurality charged. Zinc, for example, is typical of an acceptor which is doubly charged in germanium while copper is an acceptor which appears to be triply charged in germanium. Accordingly, in germanium, ion pairing between lithium and either copper or zinc is especially strong and stable against thermal dissociation, and this discovery is utilized to advantage in various illustrative embodiments of the invention.

In one illustrative embodiment of the invention, there is prepared a germanium wafer in which copper is the predominant impurity so that the wafer is p-type. Then lithium is diffused uniformly throughout the wafer to convert it completely to n-type. The presence of the copper in the wafer so enhances the solubility of lithium that enough lithium will remain stably in solution to effect a reversal in conductivity type. Thereafter, lithium is depleted from a surface layer of the wafer to effect a re-conversion of a surface layer to p-type for forming a rectifying junction in the wafer slightly below the surface.

Ion pairing between copper and lithium ions in the interior of the wafer tends to reduce the diffusivity of the lithium ions so that the rectifying junction which has been formed is stable. After appropriate electrodes are applied, the wafer which has been formed is useful for various device applications.

In another illustrative embodiment of the invention a wafer of germanium which is made p-type by the incorporation therein of atoms of zinc is treated with arsenic vapor to provide a highly doped n-type skin over a selected portion of the surface. The wafer is then saturated with lithium to convert it temporarily entirely to n-type. Thereafter, lithium is allowed to diffuse out from the surface portion unprotected by the arsenic-doped skin, whereby there is formed at this surface portion a thin p-type layer. Ion pairing in the interior tends to keep the rectifying junction formed stable. There accordingly results a wafer whose gross portion is n-type but which includes a thin p-type layer at a selected surface portion. After appropriate electrodes are applied thereto, such a wafer is useful for various device applications.

These and other illustrative embodiments are set forth in greater detail hereinafter. It is characteristic of each of the embodiments to be described that there is first prepared a semiconductive body at least one portion of which includes both a first conductivity-type determining impurity and a second conductivity-type determining impurity of opposite type which is characterized in that it forms stable ion-pair bonds with the first impurity in a useful operating temperature range. Typically, for useful operation in the range up to at least about 80° C. the two impurities should form ion pairs whose binding energy is approximately in the range between one and two electron volts. Moreover, at least the first of the two impurities should have a significant diffusion rate in the body at a temperature in the range of thermal dissociation of the ion pairs formed by ions of the first and second impurities. In particular, the diffusion rate should be sufficiently high that at a temperature which is chosen in the range of thermal dissociation to be below that at which thermal degradation of the semiconducting material is apt to become serious, the first impurity will migrate a useful distance within a reasonable heating time, for example, no more than ten hours. What is a useful distance in each case, of course, depends on the use that is to be made of the semiconductive body. In general, useful distances range from at least several hundreds Angstroms to several mils. There is then heated at least a portion of the body to the chosen temperature for the time necessary to effect the desired redistribution of the first impurity in the body. At the end of such time, for stabilizing the desired pattern, the temperature of the body is reduced below the temperature of thermal dissociation of the ion pairs to a temperature in the operating range. Because of the formation of ion pairs, the useful operating range may be made to encompass temperatures at which in the absence of ion pair formation the diffusion rate of the impurities would be so high as to make useful operation impossible.

Each of Figs. 1, 2 and 3 which constitute the drawing shows a semiconductive body which has been prepared in accordance with a different one of various embodiments of the invention.

In one embodiment of the invention, there was first prepared in the manner known to workers in the art a weakly n-type monocrystalline germanium wafer of approximately 30 ohm-centimeter specific resistivity and having dimensions approximately 300 mils by 100 mils by 50 mils. There was then electroplated over the entire surface a barely visible copper film less than one mil thick and the body was thereafter heated to 850° C. in an inert atmosphere of dry helium for approximately fifteen minutes during which time copper diffused throughout the germanium body. The body at this point had an average

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concentration of approximately 5 times 10^{18} copper atoms per cubic centimeter and was p-type with a specific resistivity of approximately .2 ohm-centimeter. Residual surface copper was removed by grinding. Then metallic lithium particles were positioned over one of the broad surfaces of the body and the body was heated in an inert atmosphere of dry helium for approximately thirty seconds at about 500° C. as a result of which the lithium was fused to such surface. This step was repeated to fuse lithium to the other broad surface of the body. Thereafter the wafer was sealed in an evacuated quartz tube and heated to about 350° C. for approximately two and a half hours, whereby lithium was diffused throughout the body. The surface of the body was then ground and etched to a high polish in the manner known to workers in the art. At the end of this operation, the thickness of the wafer had been reduced to about 40 mils. Moreover, the wafer was now n-type with a specific resistivity of about .5 ohm-centimeter. Then the wafer was positioned in a quartz jar including glycerine and heated to about 100° C. for an hour and then removed. This was a temperature sufficiently high that thermal dissociation forces overcame the coulombic attraction forces of the pairing between lithium and copper ions. It is also a temperature at which, in germanium, lithium diffuses readily and copper only slightly. As a result, this step had the effect of depleting lithium from the surface regions of the body whereby there was formed over the body a thin p-type surface layer. It was estimated that the rectifying junction formed was .1 mil below the surface of the body.

The resultant structure was then adapted for use as a photovoltaic cell by grinding away a portion of the p-type lithium-depleted layer to expose there the lithium-rich n-type interior and then providing substantially ohmic low resistance connections separately to the p-type layer and the exposed n-type region in a manner familiar to workers in the art. In Fig. 1 there is shown the end product. It comprises a germanium wafer 10 which includes an n-type gross portion 11 which is almost completely enclosed within a p-type skin 12. The thickness of the skin is shown on a greatly enlarged scale. Electrodes 13 and 14 make separate connection to the two regions of opposite conductivity type.

The resultant device was found to have photoelectric properties. Moreover, sufficient lithium was found to remain stably in solution in the interior of the body to maintain such region n-type in spite of the tendency of lithium ordinarily to precipitate out of n-type material. This enhanced solubility of lithium is largely attributable to the presence there of copper, each ionized atom of which has a triple negative charge in germanium and so is able to form stable ion pairs with as many as three ionized lithium atoms. Additionally, the formation of such ion pairs decreased the diffusivity of the lithium to such an extent that the rectifying junction formed in the body was stable for relatively long periods of time at temperatures well above temperatures at which lithium normally migrates appreciably. As still a third effect, it was found that the presence of lithium had the effect of enhancing considerably the lifetime of the minority carriers in the body above what would be expected for a body having so large a concentration of copper whose presence generally sharply degrades the lifetime characteristics of germanium.

It is, of course, feasible to modify the parameters of the embodiment described in various respects. In particular, for depleting the lithium, it is sufficient to heat the body to a temperature in the range of thermal dissociation at which the lithium has a diffusion rate which permits depletion of a layer of desired thickness in a reasonable heating time. Moreover, the temperature chosen for migration should be sufficiently low that the migration of the copper is not significant and that any resulting thermal degradation of minority carrier lifetime characteristics of

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the germanium body has little deleterious effect on the final semiconductive device for its intended use.

In the process described lithium was depleted from the entire surface of the body to form a p-type surface layer completely over the body and thereafter a portion of this layer was removed to expose a portion of the n-type interior of the body.

As an alternative it is feasible to limit the formation of a lithium-depleted p-type layer to selected portions of the surface of the body. As an example of an embodiment of this type, there is prepared a wafer of germanium which is p-type because of the predominance of zinc, a doubly charged acceptor. Thereafter, an n-type skin is formed over the body by heating the wafer together with some arsenic (50 micrograms) in an evacuated sealed quartz tube for ten hours at a temperature of 850° C. for vapor-solid diffusion of the arsenic into the surface of the body in the manner now known to workers in the art for forming an n-type arsenic-diffused layer over the surface of the body. Then lithium is diffused into the body for converting the interior of the body to n-type. The presence of the plurally charged zinc will increase the solubility of the lithium and make it possible for enough lithium to stay in solution to convert the interior to n-type. Thereafter, the arsenic-diffused layer is ground off those surface portions of the body to be converted to p-type conductivity. Then the wafer is heated to approximately 100° C. for about an hour under atmospheric conditions. At this temperature, the thermal dissociation forces are sufficient to overcome the coulombic attraction forces, and lithium diffuses readily. However, neither zinc nor arsenic diffuses much in germanium at this temperature. This results in the formation of a p-type depletion layer at the surface portions free of the arsenic-diffused layer because the lithium in the contiguous region of the body migrates to the surface and is lost, so the acceptor zinc becomes predominant in such region. However, migration to the surface where the arsenic-diffused layer remains is inhibited by the presence of this layer. As a consequence, there is formed in the wafer a thin p-type surface layer which forms a rectifying junction close to the surface. By forming separate low resistance ohmic connections to the p-type surface portion and the n-type surface portion, there results the semiconductive device 20 shown in Fig. 2 which has useful photoelectric properties. It comprises a germanium wafer which includes a gross interior portion 21 which is n-type, a skin portion 22 which is n+ type, and a skin portion 23 which is p-type. Electrodes 24 and 25 make separate connections to the n+ type and p-type skin portions.

It has also been found characteristic that in a thermal gradient a rapidly diffusing significant impurity in an extrinsic semiconductive crystal diffuses in the direction that best maintains space charge neutrality. In particular, in p-type material, lithium a donor, diffuses towards the hotter end of a crystal, while in n-type material it diffuses towards the colder end.

These principles may be combined with those of ion-pair formation in accordance with the invention to the provision of an intrinsic layer in a semiconductive crystal. In particular, a p-i-n silicon structure 30 of the kind shown in Fig. 3 may be provided as follows:

There is first prepared in any suitable manner known to workers in the art a monocrystalline silicon wafer which includes along its length both a relatively wide p-type zone 31 and a relatively thin n-type zone 32. Typically, the wafer may be 300 mils by 100 mils by 50 mils with the n-type zone two or three mils thick. Thereafter, lithium is diffused into the p-type zone of the body typically in the manner previously described. The amount of lithium introduced is chosen so that in the p-type zone the acceptor level remains slightly above the donor level. Little lithium will diffuse into the original n-type zone because its solubility there is low. Thereafter, an electrode which is kept heated to at least several hundred

degrees centigrade and typically 300° C. is positioned in contact with the n-type end of the body for a time chosen in accordance with the thickness desired for the intermediate intrinsic layer 33, typically several hours. This serves to establish a temperature gradient along the length of the body which is steep at the rectifying junction. As a result of this temperature gradient, the lithium in the p-type material diffuses towards the hot end of the body as far as the rectifying junction and tends to collect at the region contiguous with the junction. It does not diffuse beyond the junction into the n-type zone because there the tendency is to diffuse towards the cold end. Moreover, lithium only collects there until the unbalance between acceptors and donors is made up. Any further collection would drive this region to n-type after which the lithium would diffuse out. As a result, the region of the original p-type zone contiguous to the rectifying junction is converted to intrinsic material and the intrinsic layer continues to form in the direction of the cold end of the body so long as the temperature gradient is maintained. When the thickness of this intrinsic layer is as desired, the heated electrode is removed. If the acceptor predominant in the p-type zone has been chosen as previously described to form strong ion-pair bonds with lithium, the resultant structure is stable. Electrodes are then applied in conventional manner to the two ends of the body.

From the foregoing examples, it should be obvious that the principles of the invention have wide application. While the invention has been discussed with specific reference to the control of lithium in germanium, the principles may be extended to other known semiconductors, such as silicon, germanium-silicon alloys, and group III-group V intermetallic compounds such as indium antimonide, aluminum arsenide, and gallium antimonide. In accordance with such principles, a desired distribution of a rapidly diffusing conductivity-type determining impurity, i. e., one whose atoms fit interstitially in the crystal lattice, is achieved in any of the ways described and such distribution is stabilized by providing a second conductivity-type determining impurity of opposite type and chosen such that its ions form with ions of the first impurity bonds which remain stable in the useful operating temperature range. Advantageously, strong ion pair bonding may be realized by choosing as the second impurity one whose ions have a plural charge opposite in sign to the first impurity.

What is claimed is:

1. In the manufacture of a semiconductive device, the steps of preparing a semiconductive body at least one portion of which includes a first conductivity-type determining impurity and a second conductivity-type determining impurity of type opposite to the first impurity and which forms stable ion-pair bonds with the first impurity in a temperature range, where the first impurity has a significant diffusion rate in said body, said ion-pair bonds being stable in the operating temperature range of said device, heating at least one portion of the body to a temperature in the range of thermal dissociation of the ion-pair bonds for a time to redistribute the first impurity to form a rectifying junction in the body, said range of thermal dissociation being below the temperature at which thermal degradation of said body becomes appreciable, and thereafter reducing the temperature below the temperature of thermal dissociation of the ion-pair bonds to stabilize the rectifying junction.

2. In the manufacture of a semiconductive device, the steps of preparing a semiconductive body at least one portion of which includes a predominant concentration of a first conductivity-type determining impurity and a lesser concentration of a second conductivity-type determining impurity of type opposite to the first impurity and

which forms stable ion-pair bonds with the first impurity in a temperature range where the first impurity has a significant diffusion rate in said body, said ion-pair bonds being stable in the operating temperature range of said device, heating the body to a temperature in the range of thermal dissociation of the ion-pair bonds for a time to reduce the concentration of the first impurity in at least part of said first portion for reversing the conductivity-type of said part, said range of thermal dissociation being below the temperature at which thermal degradation of said body becomes appreciable and thereafter reducing the temperature of said body to one where stable ion-pair bonds form between said first and second impurities for stabilizing the new distribution of said first impurity in the body.

3. In the manufacture of a semiconductive device, the steps of preparing a semiconductive body which includes a predominance of a first conductivity-type determining impurity and a lesser amount of a second conductivity-type determining impurity of type opposite to the first impurity and which forms stable ion-pair bonds with the first impurity in a temperature range where the first impurity has a significant diffusion rate in the semiconductor, said ion-pair bonds being stable in the operating temperature range of said device, heating the body to a temperature in the range of thermal dissociation of the ion-pair bonds for a time to deplete a surface portion of the body of the first significant impurity for reversing the conductivity-type of said surface portion and forming a rectifying junction in the body, said range of thermal dissociation being below the temperature at which thermal degradation of said body becomes appreciable, and reducing the temperature below the temperature of thermal dissociation to stabilize the rectifying junction.

4. In the manufacture of a semiconductive device the process of claim 1 characterized in that the semiconductor is taken from the group consisting of silicon and germanium.

5. In the manufacture of a semiconductive device, the steps of preparing a germanium body at least one portion of which includes lithium and an acceptor impurity whose ions have a plural negative charge in germanium and which acceptor forms stable ion-pair bonds with the lithium, heating at least one portion of the body to a temperature in the range of thermal dissociation of the ion pairs formed by lithium and said acceptor ions for a time to cause migration of the lithium from at least part of said portion of the body, and reducing the temperature to below the range of thermal dissociation to stabilizing the new distribution of lithium in the body.

6. In the manufacture of a semiconductive device, the steps of preparing a germanium body at least one portion of which includes lithium as the predominant conductivity-type determining impurity and an acceptor whose ions form strong ion-pair bonds with the lithium, heating the body to a temperature in the range of thermal dissociation of the ion pairs for a time to cause sufficient migration of the lithium from at least part of said portion of the body for altering the conductivity-type of said part and forming a rectifying junction in the body.

7. In the manufacture of a semiconductive body, the process of claim 6 characterized in that copper is the acceptor.

8. In the manufacture of a semiconductive body, the process of claim 6 characterized in that zinc is the acceptor.

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