A process is provided for vapor growing a gallium arsenide single crystal layer on a substrate seed-crystal of gallium arsenide having a uniform electron concentration profile in the layer wherein at least two kinds of impurities of the same conductivity type are employed, one which causes autodoping to occur in the vapor-grown crystal, the other which tends to inhibit autodoping.

4 Claims, 2 Drawing Figures
FIG. 1

FIG. 2

INVENTORS
MITSUHIRO MARUYAMA
OSAMU MIZUNO
SADAO KIKUCHI

Sandra, Hopgood & Cohn, Attorneys
This invention relates to a process of incorporating impurities in a substrate seed-crystal of gallium arsenide in order to attain a uniform electron concentration profile in the vapor-grown gallium arsenide epilayer. The resulting gallium arsenide crystal may be adapted for the fabrication of Gunn effectors and other gallium arsenide devices.

The n-type impurities with which the substrate seed-crystals of gallium arsenide used for the vapor growth of gallium arsenide are doped are the elements of the Group VI of the Periodic Table, such as tellurium, sulfur and selenium and the Group IV elements, such as silicon and tin.

BACKGROUND OF THE INVENTION

In order to reduce the resistivity of the substrate, it is desirable to dope the substrate with as much impurity as is possible. However, if an epilayer is grown from the vapor phase on a tellurium-doped substrate with electron concentration more than 10 cm, for example, the electron concentration profile of the growth layer is influenced by substrate autodoping. The autodoping makes it impossible to ensure a uniform electron concentration profile throughout the growth layer. With regard to the phenomenon of "autodoping", reference is made to C.O. Thomas D. Kahng and R.C. Manz, J. Electroch., Soc. 109 (1962) 1055. If the tellurium concentration of the substrate is made low enough to prevent or inhibit the influence of the autodoping, the resistivity of the substrate is often too high for practical applications. Further, when a silicon- or tin-doped substrate is used for the vapor growth, low electron concentration and an electrically high resistance region appear in the growth layer in the vicinity of the layer-substrate interface, with the result that the grown layer thus obtained also does not have a uniform electron concentration profile.

It is thus the object of the invention to provide a process for growing a gallium arsenide single crystal layer on a substrate seed-crystal of gallium arsenide having a uniform electron concentration profile in the layer.

Other objects will more clearly appear from the following disclosure and the accompanying drawing, wherein:

FIG. 1 is a graph showing typical electron concentration profiles of gallium arsenide epilayers grown from the vapor phase on a conventional substrate seed-crystal; and

FIG. 2 is a graph showing exemplary electron concentration profile of a grown layer on a substrate seed-crystal according to the present invention.

General Statement of the Invention

The present invention is directed to a process for doping a substrate seed-crystal of gallium arsenide with impurities, which overcomes the difficulties above mentioned and makes it possible to obtain a vapor grown layer having a uniform impurity concentration profile.

The essence of the present invention is as follows: A substrate seed-crystal is employed for vapor growth which is doped with two kinds of impurities having the same conductivity type, one impurity being the type that causes autodoping into the grown layer from the substrate, the other being such as to inhibit autodoping. The concentration of the first impurity which causes autodoping is sufficiently restricted so as to preclude autodoping during the growth process, while the concentration of the other impurity that inhibits autodoping is made as high as possible. Thus, an epitaxial layer with uniform impurity concentration profile and of sufficiently low resistance is grown on the substrate.

The impurities that can cause autodoping into a grown layer are the n-type tellurium, selenium and sulfur and the p-type impurity zinc. The other kind of impurities which tends to inhibit autodoping includes silicon, tin and germanium as n-type impurities, germanium being also a p-type impurity, since the germanium conductivity type is amphoteric. There appears to be a critical concentration for tellurium, selenium and sulfur above which the substrate autodoping into the grown layer occurs, and below which the high resistance region in the growth layer in the vicinity of the layer-substrate interface appears. The critical value is not affected by the conditions of the vapor growth of gallium arsenide and is about $5 \times 10^{20}$ cm$^{-3}$. There is no critical value for silicon and tin. The high resistance region always appears in the growth layer in the vicinity of the layer-substrate interface, even if heavily silicon- or tin-doped substrate is used, although the electron concentration of the substrate has an upper limit of about $3 \times 10^{20}$ cm$^{-3}$.

This invention is advantageous where the impurity concentration of the grown layer is $5 \times 10^{20}$ cm$^{-3}$ or less if the grown layer is of the n-type. In the case where a vapor-grown layer has an impurity concentration of more than $5 \times 10^{20}$ cm$^{-3}$, the low electron concentration region in the vicinity of the layer-substrate interface does not appear, even if silicon- or tin-doped substrate is used; and, therefore, a substrate simply containing an impurity that does not cause autodoping results. This has nothing to do with the present invention. It is considered that there may be a similar concentration limit for p-type grown layer.

The invention will be more fully described hereunder with reference to the accompanying drawings.

DETAILS OF THE INVENTION

FIG. 1 graphically illustrates an example of electron concentration profile of an n-type vapor-grown layer on a conventional substrate of n-type gallium arsenide. The curve 11 represents the electron concentration profile of a substrate. The curve 13 is the electron concentration profile of the layer grown on a substrate doped with $1 \times 10^{20}$ cm$^{-3}$ tellurium, which shows occurrence of autodoping of tellurium into the grown layer, while the curve 14 represents the profile of the layer grown on a substrate doped with $1 \times 10^{20}$ cm$^{-3}$ silicon, which shows the appearance of low electron concentration region near the layer-substrate interface.

In an embodiment of the invention, a substrate seed-crystal of n-type gallium arsenide doped with both $5 \times 10^{20}$ cm$^{-3}$ tellurium and $1 \times 10^{20}$ cm$^{-3}$ silicon is employed. Referring to FIG. 2, lines 21 and 22 represent electron concentrations in the substrate seed-crystal due to silicon and tellurium, respectively, while the hatched portion represents the amount of electron concentration due to silicon in excess of that due to tellurium. On this substrate, an n-type gallium arsenide layer is grown by feeding arsenic trichloride (AsCl$_3$) gas with hydrogen gas as a carrier gas into a reaction system in which gallium heated at 850°C and the substrate heated at 750°C are placed. Line 23 of FIG. 2 represents the electron concentration profile of the layer thus obtained. Thus, by doping the substrate seed-crystal with tellurium of the critical amount, or $5 \times 10^{20}$ cm$^{-3}$, that avoids the autodoping of tellurium from the substrate into the grown layer, it is possible to obtain a vapor-grown layer with a uniform electron concentration profile. In addition to tellurium doping, by doping said substrate seed-crystal with $1 \times 10^{20}$ cm$^{-3}$ silicon that inhibits autodoping, it is possible to prevent increase in the resistivity of the substrate.

Doping the substrate seed-crystal with not only $5 \times 10^{20}$ cm$^{-3}$ tellurium and $1 \times 10^{20}$ cm$^{-3}$ silicon but also with not less than $1 \times 10^{20}$ cm$^{-3}$ tin will, like silicon, induce no autodoping, while reducing the resistivity of the substrate still further. Simultaneous doping with other different impurities may be employed to reduce the substrate resistivity or control the autodoping as desired.

For example, doping with silicon and tin both within the limit of concentration of about $3 \times 10^{20}$ cm$^{-3}$ would make it possible to enhance the electron concentration of the substrate to $6 \times 10^{20}$ cm$^{-3}$. Additional doping with tellurium and selenium both in the concentration of $5 \times 10^{20}$ cm$^{-3}$ would enable increasing the electron concentration of the substrate up to $7 \times 10^{20}$ cm$^{-3}$ without autodoping occurring in the grown layer.

As described above, the present invention makes it possible to obtain easily a vapor-grown layer of gallium arsenide having
a uniform impurity concentration profile and to control, as desired, the impurity concentration profile in the growth layer near the layer-substrate interface by varying the kinds and concentration of the impurities doped in the substrate seed-crystal.

It should be understood that the present invention is not limited to the embodiment above described, but, of course, many other applications are possible without departing from the spirit of this invention.

What is claimed is:

1. A process for vapor growing gallium arsenide which comprises, doping a substrate of gallium arsenide single crystal with at least one impurity selected from the group consisting of tellurium, selenium and sulfur each in an amount of about $5 \times 10^{19} \text{m}^{-3}$ and at least one other impurity from the group consisting of silicon and tin, each in an amount of less than about $3 \times 10^{20} \text{cm}^{-3}$, and vapor-growing an n-type gallium arsenide single crystal having impurity concentration of less than $5 \times 10^{19} \text{m}^{-3}$ on said substrate of gallium arsenide single crystal.

2. The method of claim 1, wherein one impurity is tellurium, and wherein the other impurity is silicon.

3. The method of claim 1, wherein one impurity is tellurium, and wherein silicon and tin together comprise the other impurity.

4. In a process for vapor growing a gallium arsenide single crystal layer on a substrate seed-crystal of gallium arsenide having a uniform electron concentration profile in the layer, the improvement which comprises the steps of doping said substrate seed-crystal with at least two kinds of impurities having the same conductivity type, one being able to cause autodoping to occur in the vapor-grown crystal which is selected from the group consisting of tellurium, selenium and sulfur each in an amount of about $5 \times 10^{20} \text{cm}^{-3}$, the other tending to inhibit autodoping which is selected from the group consisting of silicon, tin and germanium, and vapor-growing a gallium arsenide single crystal having impurity concentration of less than $5 \times 10^{19} \text{m}^{-3}$ on said substrate seed-crystal of gallium arsenide single crystal.