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(54) Manufacture of electronic devices comprising cadmium mercury telluride involving vapour phase deposition

(57) In the manufacture of an electronic device, for example an infrared detector, from a crystalline layer (11) of cadmium mercury telluride, as illustrated in Figs. 4 & 5, a surface (9') of a substrate (10) is irradiated to apply a heat pulse (20) which removes surface material (8) so as to leave a clean surface (9) suitable for the growth of the crystalline layer (11). During the application of the heat pulse (20) and the deposition of the layer material (11), the substrate (10) is maintained in a non-oxidising ambient, for example a stream (5) of hydrogen, nitrogen or a noble gas. This gas (5) may carry Hg vapour to the substrate (10'), and volatile Cd and Te compounds may be introduced into the gas stream during the deposition. Although at least most of the material for the cadmium mercury telluride layer is deposited below 550°C (and preferably below 450°C), the substrate surface (9') may be heated rapidly by the pulse (20) to a temperature in excess of 800°C (even in excess of 1000°C) to permit the removal of silicon dioxide surface layers (8) from silicon substrates (10). Due to its short duration, the pulse (20) can effect the cleaning without degrading the quality of the deposited layer (11) or degrading circuit elements (55) in the substrate (10). In a modification a buffer layer (12) of CdTe may be grown on the clean surface (9) before the cadmium mercury telluride layer (11), after which the cadmium mercury telluride layer (11) may be grown on this CdTe buffer layer (12) by liquid phase epitaxy. The heat pulse may be produced by switching a radiant heat source directed at the surface of the substrate or by directing a pulsed laser. The substrate treated may be monocrystalline silicon or monocrystalline germanium.

Electronic devices manufactured may be photoconductive infrared detectors, photodiode infrared detectors and bipolar transistors.

Fig.4.

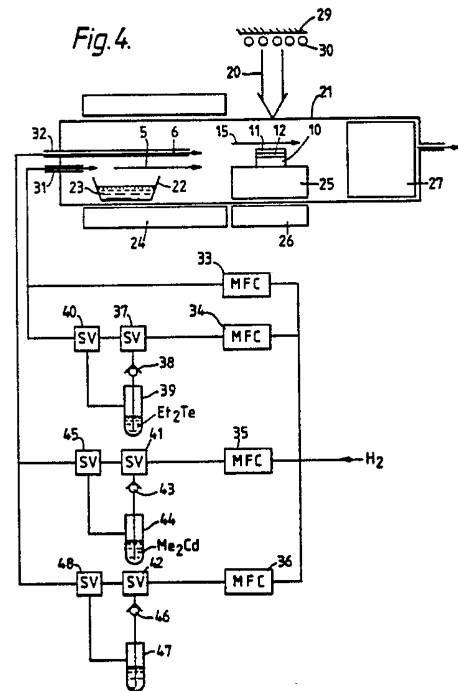

Fig.5.

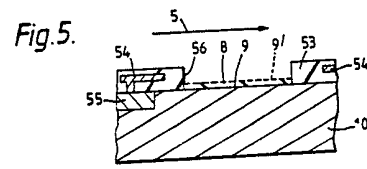

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Fig.1.

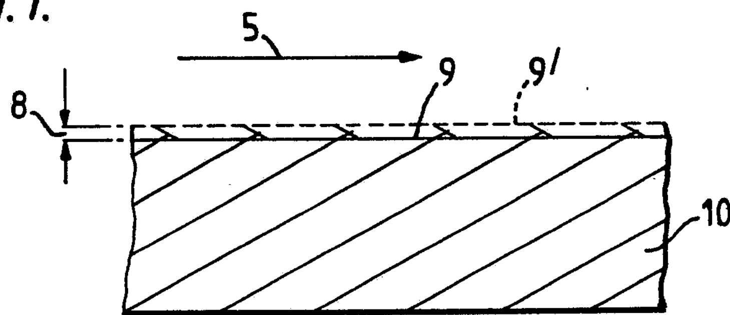


Fig.2.

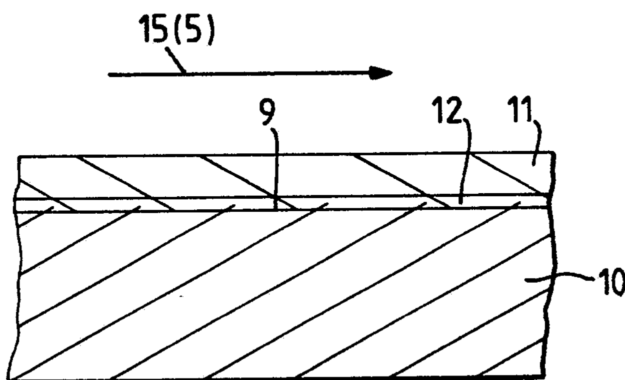
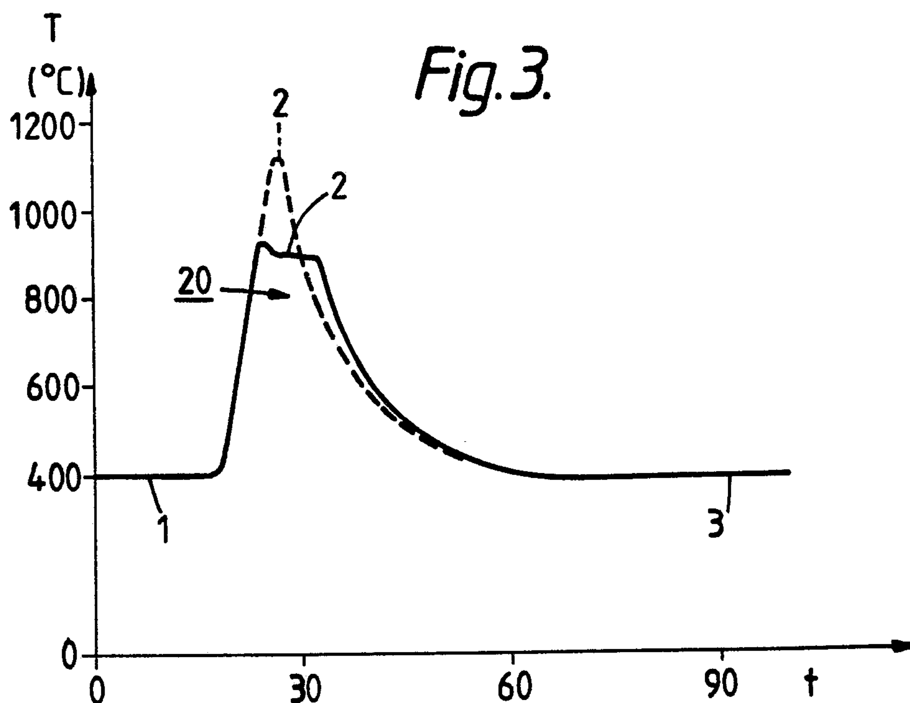


Fig.3.



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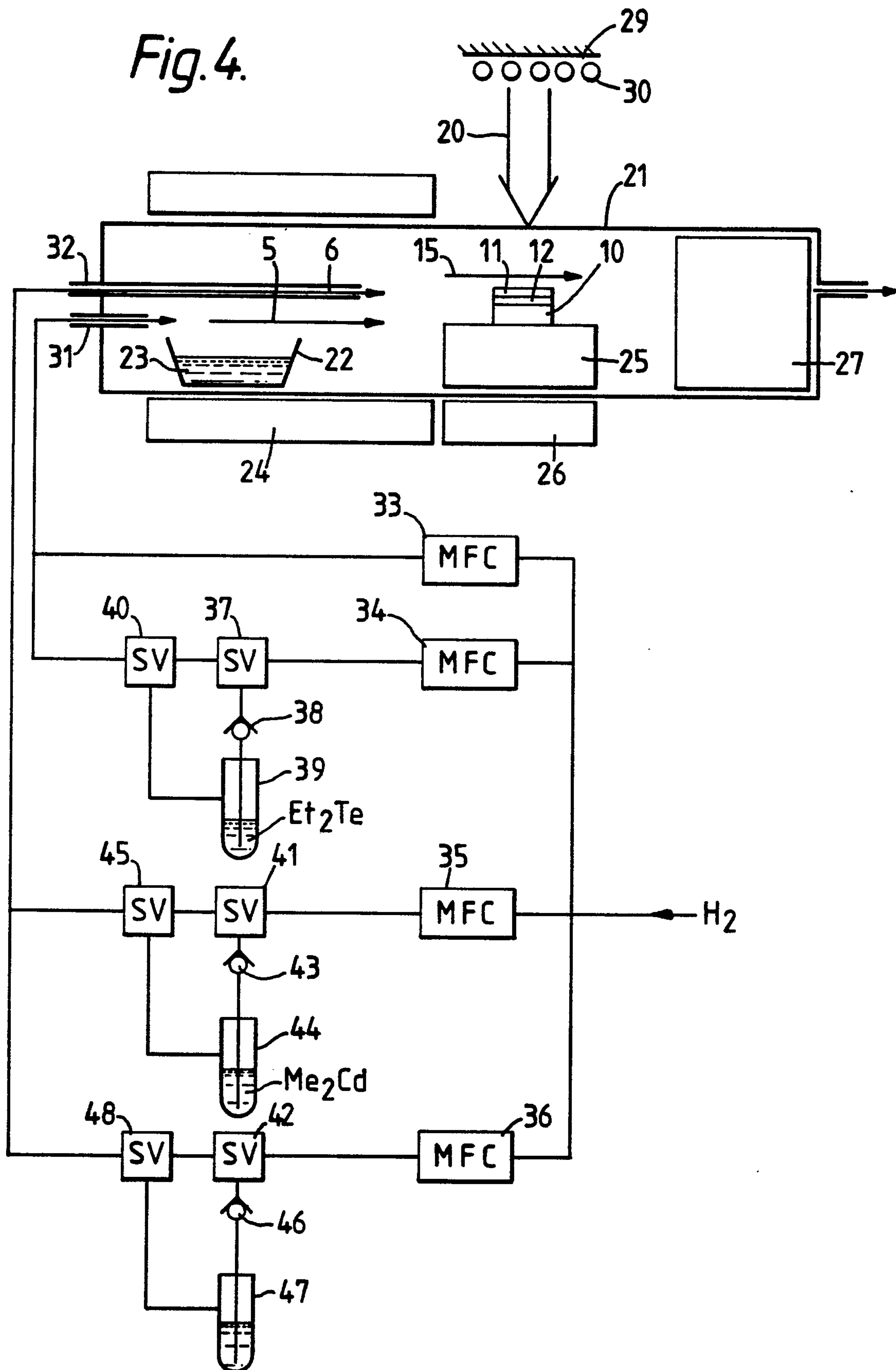

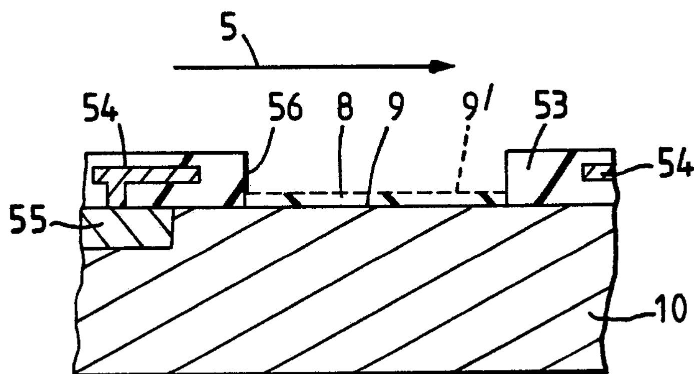
Fig.5.
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9'
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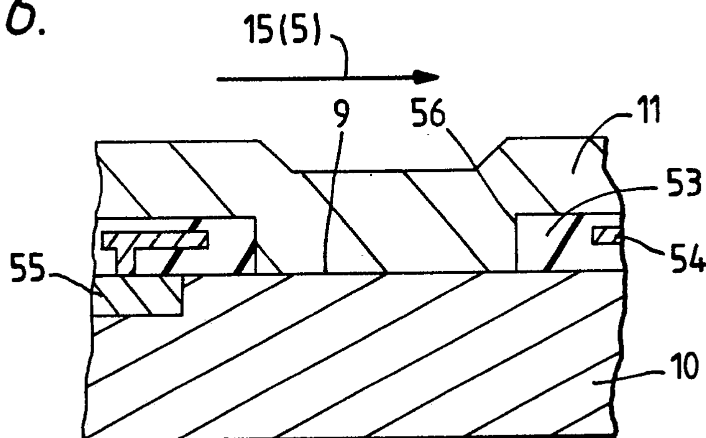
Fig.6.
15(5)
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11
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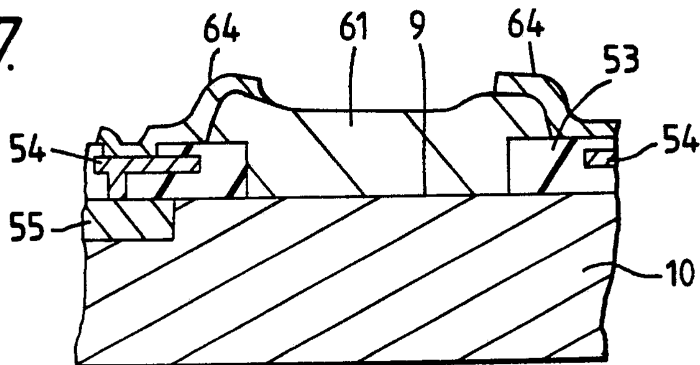
Fig.7.
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MANUFACTURE OF ELECTRONIC DEVICES
COMPRISING CADMIUM MERCURY TELLURIDE

This invention relates to methods of manufacturing electronic devices comprising crystalline cadmium mercury telluride grown on a substrate, and involving deposition of material from a vapour phase onto a surface of the substrate. Electronic devices manufactured using the crystalline material may be, for example, photoconductive infrared detectors, photodiode infrared detectors, and bipolar transistors.

Published United Kingdom patent application GB-A-2 146 663 describes a method of manufacturing an electronic device such as an infrared detector comprising cadmium mercury telluride, in which a gas stream comprising mercury, cadmium and tellurium is passed over a substrate inside a reactor vessel while a surface of the silicon substrate is heated to a temperature below 550°C, a crystalline layer comprising cadmium mercury telluride being grown on the surface of the substrate from the deposited material. Thereafter, further device fabrication steps are effected using at least part of the crystalline layer to provide a part of the electronic device. The whole contents of GB-A-2 146 663 are hereby incorporated as reference material into the present specification.

Crystalline cadmium mercury telluride ($Cd_xHg_{1-x}Te$) is a difficult material to grow with a desired composition. Several processes which have been tried and/or used for its growth are described in GB-A-2 146 663, and a particularly advantageous method is disclosed in which very thin alternate layers of cadmium telluride and mercury telluride are grown sequentially on a cadmium telluride substrate and are interdiffused whilst growing to give the desired composition (x value) for the $Cd_xHg_{1-x}Te$ layer. This is achieved by switching on and off a supply of a volatile cadmium compound (for example an alkyl) in a gas stream (for example of hydrogen) which flows over the substrate and which comprises a volatile tellurium compound (for example an alkyl) and mercury vapour. CdTe is deposited in preference to HgTe when the volatile Cd compound supply is switched on.

A modified process for crystalline growth is disclosed in published PCT international patent application WO-A-86/02951 in which lower substrate temperatures can be used by providing photolytic decomposition of the alkyls in the gas stream. In order to prevent the deposition of the CdTe material from the vapour phase as a dust on the substrate due to premature nucleation in the gas stream, the carrier gas comprises at least 50% by volume of an inert gas such as He, Ne, Ar, N_2, CH_4, C_2H_6 and mixtures thereof. The whole contents of WO-A-86/02951 are hereby incorporated as reference material into the present specification.

In the particular methods disclosed in GB-A-2 146 663 and WO-A-86/02951, a cleaned substrate of CdTe is placed on a susceptor in the reactor vessel. Typical temperatures used in these growth processes are: 190 to 320°C (degrees Celsius) for the walls of reactor vessel and for a mercury reservoir, and 400 to 430°C or 200 to 350°C for the substrate. Instead of the substrate being CdTe or another II-VI compound or mixed II-VI alloy, it is mentioned in both GB-A-2 146 663 and WO-A-86/02951 that the substrate may be of silicon, germanium, indium antimonide, gallium arsenide or another semiconductor material, or of spinel, sapphire or any other known substrate material.

The use of substrates of silicon, germanium and indium antimonide is particularly attractive because of the optical transmission and absorption properties of these materials for infrared detectors of cadmium mercury telluride. The possibility of fabricating circuits in silicon, germanium and gallium arsenide also renders these materials attractive because such substrates may then be used for processing electrical signals associated with the cadmium mercury telluride devices. However it has proved difficult to grow crystalline cadmium mercury telluride of adequate crystalline quality and uniform desired composition on substrates of these materials other than CdTe, and in many cases the adhesion of the deposited layer to the substrate is poor.

Similar difficulties are experienced when attempting to grow the cadmium mercury telluride on such substrates using other vapour

phase deposition processes, for example molecular beam epitaxy and evaporation in a vacuum.

According to the present invention there is provided amethod of manufacturing an electronic device comprising cadmium mercury telluride, in which material comprising mercury, cadmium and tellurium is deposited from a vapour phase onto a surface of a substrate inside a reactor vessel while the surface of the substrate is heated to a temperature below 550°C (or preferably even below 450°C), a crystalline layer comprising cadmium mercury telluride being grown on the substrate from the deposited material, and further device fabrication steps are effected using at least part of the crystalline layer to provide a part of the electronic device, which method is characterised by (a) irradiating the surface of the substrate to apply a heat pulse which removes surface material from the substrate and thereby to leave a clean surface of the substrate suitable for the growth of the crystalline layer, (b) thereafter depositing the material for the crystalline layer on the clean surface, and (c) maintaining the substrate in a non-oxidising ambient in the reactor vessel during steps (a) and (b).

By thus applying in accordance with the present invention such a heat pulse by irradiating the substrate surface in situ in the reactor vessel, a clean surface of the substrate suitable for the growth of the crystalline layer is obtained by removal of surface material while still permitting low temperatures in the deposition of the material for the cadmium mercury telluride layer. This in-situ cleaning by the heat pulse removes contaminants which may be present on the substrate surface prior to the growth, and it permits crystalline growth of cadmium mercury telluride (and an appropriate buffer layer, if so desired) on substrates of semiconductor materials such as silicon and germanium which normally have thin oxide surface layers tending to weaken the adhesion of the cadmium mercury telluride layer to the substrate and/or to degrade the crystalline quality of the layer. In the case of non-semiconductor substrates such as sapphire, the heat

pulse drives off adsorbed water vapour and other contaminants from the irradiated surface of the substrate.

The term 'heat pulse' as used herein, should be understood to mean a relatively short duration application of heat, normally for less than two minutes and preferably less than 30 seconds, to raise temporarily the temperature of the substrate as required to effect the cleaning. Thus, prior to the heat pulse, the substrate may be maintained at a low temperature and its temperature rises rapidly and then falls rapidly with the heat pulse. In this way diffusion and/or outgassing from the substrate are at least substantially mitigated. This is particularly advantageous in the case of semiconductor substrates, because both silicon and germanium are dopants for cadmium mercury telluride, and regions of circuit elements which may be present in the semiconductor substrate may diffuse or become degraded in some other way if they were to be heated at a high temperature for any prolonged period of time. Furthermore, depending on the vapour phase deposition system used with appropriate reactant sources of cadmium, tellurium and mercury, the heat pulse (if it is sufficiently rapid and short) may even be applied after introducing the reactants into the reactor vessel.

The substrate within the reaction vessel may be at ambient-temperature prior to the application of the heat pulse. However, it may be desirable to preheat the substrate to an elevated temperature prior to the application of the heat pulse, for example to reduce the heating power required to be switched to apply the heat pulse. The elevated temperature to which the substrate may be raised will be chosen to be below the minimum temperature(s) at which cleaning occurs and at which degradation may occur to any semiconductor circuit elements or reactants in the vapour phase which may already be present. However in order to provide some thermal stability in the absence of the heat pulse, the prior elevated temperature may be similar to the subsequent, desired deposition temperature for the cadmium mercury telluride layer. When the heat pulse is generated by a

radiant-heat source, the heating to the prior elevated temperature and the subsequent deposition temperature may be accomplished using the same radiant heater and abruptly switching it temporarily to a higher power level to generate the heat pulse. However, different
5 heating means may be used for the different temperatures, and the temperature of the substrate prior and subsequent to the heat pulse may be determined by one means, and the heat pulse may be generated by another means. Instead of using a radiant-heat source, a suitable heat pulse can be produced by absorption of energy from a
10 pulsed laser.

The heat-pulse cleaning treatment is remarkably effective even with silicon substrates requiring high temperatures to remove silicon dioxide surface layers. In general it has been found that with radiant heaters the minimum duration for the heat pulse of the
15 cleaning step employed on silicon substrates in various experiments was imposed by the power available for the radiant heaters and by the thermal inertia of the reactor vessel, and not by any limit to the effectiveness of the cleaning step. Heat pulse duration times of less than 15 seconds, and a reduction in the time taken for the
20 substrate temperature to rise to and fall from the heat-pulse cleaning temperature may advantageously be employed in a method in accordance with the present invention. Suitably short and rapid heat pulses may be achieved with a radiant heating arrangement adapted from a radiantly heated rapid annealing furnace such as
25 that described in, for example, published United Kingdom patent application GB-A-2 136 937 (PHB 32964), the whole contents of which are hereby incorporated as background material in the present specification. However an even more rapid temperature change and short pulse duration can be achieved using a high-intensity pulsed
30 laser beam or electron beam. In this case, by using very short duration laser or electron pulses, the high temperature heating can be limited to a surface layer of the substrate so that the overall substrate temperature remains low, the heat can rapidly dissipate into the bulk of the substrate at the end of the pulse, and so the
35 temperature of the clean surface also rapidly falls.

In a particular embodiment in accordance with the invention involving deposition of the material for the layer from one or more gas streams, the non-oxidising ambient in which the substrate is maintained during the application of the heat pulse is provided by a gas which forms part of the gas stream during said deposition and may serve to carry one or more of the mercury, cadmium and tellurium constituents to the substrate during said deposition. Because of its chemical reducing properties, hydrogen may be a particularly suitable non-oxidising gas, although an inert gas such as nitrogen and helium or another noble gas is also attractive. The mercury may be supplied to the gas stream by passing the non-oxidising gas or another carrier gas over a heated reservoir of liquid mercury, either inside or outside the reactor vessel, but outside the area heated by the heat pulse. The mercury vapour may be present in the gas stream during the heat pulse. After the end of the heat pulse, the tellurium may be introduced into the gas stream as a hydride or alkyl of tellurium or as another volatile tellurium compound. After the temperature of the surface of the substrate heated by the heat pulse has fallen to below 500°C, the cadmium may be introduced into the gas stream as a hydride or alkyl of cadmium or as another volatile cadmium compound.

Deposition of material on the clean surface of the substrate may be commenced from reactants in the gas stream while the substrate temperature is still falling at the end of the heat pulse. Especially when a buffer layer of suitable material is first grown on the clean surface, this deposition may commence at a temperature above 550°C. However, in order to obtain a good quality cadmium mercury telluride layer, the material for at least most of this cadmium mercury telluride layer is preferably deposited with a substrate surface temperature stabilised at a level below 450°C.

According to another aspect of the present invention there is provided a method of manufacturing an electronic device comprising cadmium mercury telluride, in which a gas stream comprising cadmium and tellurium is passed over a substrate inside a reactor vessel

while a surface of the substrate is heated so as to deposit a cadmium telluride layer on the substrate, after which an epitaxial crystalline layer of cadmium mercury telluride is grown on the cadmium tellurium layer and further device fabrication steps are effected using at least part of the crystalline layer of cadmium mercury telluride to provide a part of the electronic device, which method is characterised by (a) irradiating the surface of the substrate to apply a heat pulse which removes surface material from the substrate and thereby to leave a clean surface of the substrate suitable for the growth of the cadmium telluride layer, (b) thereafter depositing the cadmium telluride layer on the clean surface, and (c) maintaining the substrate in a stream of non-oxidising gas in the reactor vessel during steps (a) and (b).

The heat pulse may be applied as already described herein. After depositing the cadmium telluride layer the composition of the gas stream may be changed to deposit from the gas stream at least most of the material for the cadmium mercury telluride layer, when the temperature of the surface of the substrate has fallen to below 550°C (and preferably below 450°C). In an alternative process the substrate with the cadmium mercury telluride layer is removed from the reactor vessel and the cadmium mercury telluride layer may be grown thereon by liquid phase epitaxy.

These and other features in accordance with the present invention will be illustrated further in embodiments of the invention now to be described, by way of example, with reference to the accompanying diagrammatic drawings, in which:

Figures 1 and 2 are cross-sectional views of a substrate on which a cadmium mercury telluride layer is provided, at two stages in the manufacture of an electronic device by a method in accordance with the invention;

Figure 3 is an example of the change in temperature (T) of the substrate surface with time (t) such as occurs during the stages of manufacture illustrated in Figures 1 and 2;

Figure 4 is a schematic representation of a longitudinal section through a vapour-phase epitaxial reactor and of its gas

supply system, in which reactor the stages of Figures 1 and 2 can be performed, and

Figures 5 to 7 are cross-sectional views of another substrate on which a cadmium mercury telluride layer is provided, at three stages in the manufacture of an electronic device by a method in accordance with the invention.

It should be noted that the Figures are diagrammatic and not drawn to scale, the proportions of parts of these drawings having been exaggerated or diminished for the sake of convenience and clarity in the drawings. The same reference signs as used in one embodiment are generally used when referring to corresponding or similar parts in the other embodiments.

At the stage of manufacture illustrated in Figure 2, a gas stream 15 comprising mercury, cadmium and tellurium is passed over a monocrystalline substrate 10 (for example of silicon or germanium) inside a reactor vessel 21 (see for example Figure 4) while a surface 9 of the substrate is heated to a temperature below 550°C so as to grow a crystalline layer 11 of cadmium mercury telluride on the substrate 10 by deposition of material from the gas stream 15. If so desired, the material may be deposited as very thin alternate layers of CdTe and HgTe which interdiffuse to form the cadmium mercury telluride layer 11, as described in GB-A-2 146 663. As illustrated in Figure 2, a buffer layer 12 of, for example CdTe, or HgTe or any other compatible material may be grown initially on the surface 9 of the substrate 10 from the gas stream 15, before the cadmium mercury telluride layer 11. With a silicon substrate, the surface 9 may have a <100> crystal orientation, or it may be, for example, about 2 degrees off a <111> orientation.

After the stage illustrated in Figure 2, further device fabrication steps are effected in known manner, using at least part of this crystalline layer 11 of cadmium mercury telluride to provide a part of the electronic device. The device may be, for example, an infrared detector or a transistor. Some of these further steps may be effected in the same reactor vessel 21 as the

growth of the layer 11. Thus, for example, a passivating layer of CdTe may be deposited on the layer 11 by appropriately changing the constituents in the gas flow 15. However, most of the further device fabrication steps are performed outside the reactor
5 vessel 21, for example patterning the layer 11 into a desired shape for a device element, depositing metal electrodes contacting the cadmium mercury telluride, and perhaps p-n junction formation in the cadmium mercury telluride layer 11. The further processing may also be effected on the substrate 10, for example by shaping the
10 substrate 10 to form an appropriate optical element for the device.

In accordance with the present invention an early stage illustrated in Figure 1 is effected in the reactor vessel 21 before depositing the material to grow either the cadmium mercury
15 telluride layer 11 or the CdTe layer 12. In this stage a heat pulse 20 (see Figures 3 and 4) is applied to the surface 9' of the substrate 10 by irradiation so as to remove surface material 8 from the substrate 10 and thereby to leave the substrate 10 with a clean surface 9 which is suitable for the growth of the crystalline
20 layers 11 and 12. The heat pulse is applied while maintaining the substrate in a stream 5of non-oxidising gas in the reactor vessel 21. The material 8 vaporized by the heat pulse 20 is carried away by the gas stream 5. Thereafter the material from the gas stream 15 is deposited on the clean surface 9 to provide at least
25 most of the material for the crystalline layer 11 of cadmium mercury telluride when the temperature of the surface 9 of the substrate 10 has fallen to below 550°C, preferably below 450°C.

As indicated by the reference signs 15 and 5 in Figure 2, the non-oxidizing gas 5 of Figure 1 forms part of the gas stream 15
30 during the deposition, and this non-oxidising gas 5 may serve to carry one or more of the mercury, cadmium and tellurium to the substrate 10 during the deposition. In this manner a flow of the non-oxidising gas 5 is maintained over the substrate 10 from the cleaning of its surface 9',9 by the heat pulse to the
35 deposition of the material to form the CdTe layer 12 and the

cadmium mercury telluride layer 11. One example of a particular arrangement is illustrated in Figure 4 in which the non-oxidising gas flow 5 forms a part of the gas stream 15 carrying Hg vapour from a reservoir 22 of liquid mercury 23 and (depending on the gas
5 flow switching) possibly also a volatile Te compound from a bubbler 39.

In the case of a substrate 10 of silicon the surface layer 8 may comprise a naturally formed skin of silicon dioxide. However, it is preferable to effect an initial cleaning of the surface 9'
10 before placing the substrate 10 in the reactor vessel 21, so as to remove such a naturally formed skin and contaminants from the surface 9' and to form at the surface 9' a protective thin oxide layer which is substantially free from contaminant species. A suitable cleaning process using solutions containing hydrogen
15 peroxide is described in the journal article RCA Review Vol. 31, pages 187 to 205, June 1970. By using such a pre-clean process the surface 9' of the silicon substrate 10 is coated with a protective thin surface oxide layer (about 1nm thick) which is substantially free from contaminant species, in particular carbon and metals.
20 The surface oxide layer reduces risk of surface contamination while the substrate 10 is being placed in the reaction vessel 21 and during the (rapid) rise in temperature of the substrate surface 9' at the beginning of the heat pulse 20. The whole contents of this RCA Review article are hereby incorporated as reference material in
25 the present specification. Similar protective surface layers of an oxide or other material may be established in various ways on substrates 10 of germanium or other materials prior to the heat-pulse cleaning.

Figure 3 illustrates the effect of two examples of a heat
30 pulse suitable for removing surface material 8 (including such a thin protective silicon dioxide layer) from the surface of a silicon substrate 10. The temperature of the surface 9',9 of the silicon substrate 10 is raised by the heat pulse 20 to a temperature 2 in excess of 800°C (degrees Celsius): in one example
35 to about 900°C for a time of about 10 seconds, taking the units of

the t axis as corresponding to seconds; and in another example to about 1100°C for a few seconds. Such heating pulses 20 remove the thin surface layer of silicon dioxide and one or more monolayers of silicon from the substrate surface. It is thought that at these 5 temperatures the silicon dioxide is reduced to silicon monoxide by the underlying silicon and that this silicon monoxide then vaporises. Lower temperature heat pulses are sufficient for the surface removal treatment on a germanium substrate. A minimum duration for the pulse 20 for entirely removing such oxides 10 increases with increase in the thickness of the oxide.

The heat pulse 20 can be produced by switching a high power radiant heat source 30 (see Figure 4) directed at the surface 9' of the substrate 10. At the end of the heat pulse 20 the temperature of the substrate surface falls to a level 3 which is in the region 15 of 400°C in the example of Figure 3, and at this temperature 3 the deposition is performed for most of the cadmium mercury telluride layer 11. The temperature level 3 is preferably maintained using another heating means than that to produce the pulse 20, for example using the heating means 25 and 26 illustrated 20 in Figure 4. This same heating means 25 and 26 may be used to raise the temperature of the substrate 10 from ambient to an elevated temperature 1 prior to the application of the heat pulse 20. As illustrated in Figure 3 the temperature levels 1 and 3 may be the same, the temperature of the substrate surface 9' 25 being simply changed by the heat pulse 20.

Figure 4 diagrammatically shows one example of an apparatus which can be used to clean the substrate 10 and grow the cadmium mercury telluride layer 11 on the clean surface 9 of substrate 10 by a metallo-organic vapour phase epitaxy process. The apparatus 30 comprises a tubular silica reactor vessel 21 having three zones. A boat 22 containing mercury 23 is located in a first zone which may be heated by, for example, a tubular resistance furnace 24. A cleaning and growth zone contains a silicon carbide coated graphite susceptor 25 which rests on the bottom of the reactor tube 21 and 35 which may be, for example, radiantly heated by a resistively-heated

semi-tubular furnace 26. The heat pulse 20 may be produced by a higher power radiant heat source 30, for example in the form of a bank of high power tungsten lamps or tungsten halogen lamps. The growth zone is physically separated from the first zone by a sufficient distance to ensure that not only the tubular and semi-tubular furnaces 24 and 26 do not heat the susceptor 25 and boat 22 respectively, but also that the mercury boat 22 is outside the zone of heating of the heat pulse 20.

A third zone at the exit end of the reactor tube 21 is spaced from the second zone and is unheated. It may contain a closely-fitting removable liner 27 which serves as a "dump-tube" on which unreacted material (for example mercury), reaction by-products, and even possibly the vaporized surface material 8 may be deposited. Such a liner 27 simplifies the problem of cleaning the reactor tube 21 after a deposition run. Material deposited in the growth zone on the wall of the reactor tube 21 is transferred onto the internal surface of the liner 27 by placing a tubular furnace around the growth zone of the reactor tube 21, passing a hydrogen stream through the tube 21 (from left to right in Figure 4) and heating the growth zone to a temperature which is 300 to 400 degrees Celsius above the temperature prevailing in the reaction zone during the deposition process.

The walls of the reactor tube 21 in the first zone and the mercury 23 present in the boat 22 may be heated by the tubular furnace 24 to a temperature of from 220 to 250°C. The semi-tubular furnace 26 may comprise a ceramic semi-tube provided on its inside surface with longitudinally extending channels in which a helical wire resistance element is disposed. This may heat the substrate 10 to about 400°C. The bank of lamps 30 may comprise a water-cooled reflector 29 and the lamps themselves may be cooled by blown air.

In the example illustrated in Figure 4, the non-oxidising gas flow 5 is of high purity hydrogen, for example palladium-diffused hydrogen. It is supplied to the reactor vessel 21 via the mass flow controller 33 before and during the application of the heat

pulse 20 and during the growth of the layers 11 and 12. In the form illustrated in Figure 4 this hydrogen gas flow 5 enters the reactor vessel 21 via an injection tube 31 upstream of Hg bath 22 and so carries the Hg vapour to the substrate 10. However the end
5 of the injection tube 31 may be located downstream of the bath 22 and a separate hydrogen gas flow may be provided to carry the Hg vapour; the Hg bath 22 may even be located outside the reactor vessel 21.

A variety of different volatile compounds of Cd and Te may be
10 used to supply the Cd and Te constituents for the layer 11. In one example, hydrides of Cd and Te are used. Figure 4 illustrates another example using alkyls of Cd and Te. Thus, diethyl telluride and dimethyl cadmium are shown being introduced into the reactor vessel 21 in the form of a current 5 of hydrogen and diethyl
15 telluride vapour and a current 6 of hydrogen and dimethyl cadmium vapour through respective injection tubes 31 and 32 which extend through one end of the reactor 21.

Figure 4 diagrammatically shows one example of a gas supply system which may be used with the reactor 21. Palladium-diffused
20 hydrogen is supplied to each of four mass flow controllers 33, 34, 35 and 36. The diethyl telluride vapour is generated by passing hydrogen through the mass flow controller 34, a three-way solenoid valve 37 and a non-return valve 38 to a bubbler 39 containing diethyl telluride liquid. The mixture of the hydrogen and diethyl
25 telluride vapour produced in the bubbler 39 flows through a three-way solenoid valve 40 and is then diluted with hydrogen supplied through the mass flow controller 33, the resulting mixture entering the reactor 21 through the tube 31.

The hydrogen streams from the mass flow controllers 35 and 36
30 pass through respective three-way solenoid valves 41 and 42. When the solenoid valve 41 is in a first position, the hydrogen flow through the valve 41 passes through a non-return valve 43 to a bubbler 44 containing dimethyl cadmium, and the current of hydrogen and dimethyl cadmium vapour passes through a three-way solenoid
35 valve 45 in a first position to the injection tube 32 which

terminates in the reactor 21 between the downstream end of the boat 22 and the susceptor 25. When the three-way solenoid valve 41 is in a second position, the valve 45 is also in a second position and then the hydrogen stream from the mass flow controller 35 by-passes the bubbler 44. The hydrogen stream from the mass flow controller 36 passes through the three-way solenoid valve 42 either through a non-return valve 46 to a bubbler 47 which may contain a dopant compound and to a three-way solenoid valve 48, or directly to the three-way solenoid valve 48. The gas currents from the valves 45 and 48 are combined and enter the reactor 21 through the tube 32.

The bubblers 39, 44 and 47 are each kept at a stable temperature, for example 25°C, by means of a water bath (not shown) in order to keep the vapour pressures of the respective alkyls constant. The apparatus may be designed to operate with the gas pressure inside the reactor 21 comparable to atmospheric pressure or significantly lower than atmospheric pressure, if so desired.

A particular operating sequence will now be described, by way of example. After the preliminary cleaning and surface-oxidation treatment the substrate 10 is placed on the susceptor 25 in the reactor vessel 21. A flow 5 of hydrogen is passed over the substrate 10 via the controller 33 and tube 31, and the substrate 10 is heated to temperature level 1 (Figure 3) by the heater 26. Any hydrogen flow from the controllers 34, 35 and 36 is routed by the solenoid valves so as to bypass the bubblers 39, 44 and 47. The heat pulse 20 is then applied by abruptly switching the radiant heat source 30, while maintaining the hydrogen flow 5. After the end of the heat pulse 20, the tellurium alkyl is introduced into the reactor 21 by switching the valves 37 and 40 and adjusting the flow controllers 33 and 34 to provide a desired flow rate. As a result a buffer layer 12 of HgTe may be grown on the clean surface 9 of the substrate 10. When the temperature of the surface 9 of the substrate 10 has fallen to below 500°C, the cadmium alkyl may be introduced into the gas stream 15 by switching the valves 41 and 45 and adjusting the flow controllers 33, 34

and 35 as desired. The cadmium supply may be switched on and off by the valves 41 and 45 so as to produce alternate thin layers of CdTe and HgTe which interdiffuse to form the desired cadmium mercury telluride composition for the layer 11. A thicker uppermost layer of CdTe may be grown to passivate the upper surface of the layer 11.

The layer 11 may be doped as desired by appropriately switching the valves 42 and 48. It will be evident that, by providing one or more additional sets of a mass flow controller, bubbler or other source, and associated valves, other materials may be deposited as, for example a buffer layer 12 or for example an antireflection coating at the upper surface of the final layer structure on the substrate 10.

It will be evident that many modifications are possible within the scope of the present invention. Thus, for example, instead of a radiant heat source for the heat pulse 20, a pulsed laser may be used. With such a laser, the heat pulse 20 can be of much shorter duration, for example the units of the t axis in Figure 3 may be read as corresponding to milliseconds in such a case, and a much higher temperature level 2 than that shown in Figure 3 can be obtained. The laser pulses may be repetitive during the cleaning stage of Figure 1. In this manner the direct heating of the substrate 1 may be restricted to the vicinity of the surface 9',9 so that at the end of the pulse the bulk of the substrate 10 can act as a heat sink rapidly cooling the clean surface 9 for the deposition. With suitably fast laser pulses and appropriate volatile compounds of tellurium and/or cadmium, the heat pulse 20 may even be applied when passing the deposition gas stream 15 over the substrate 10, the heat pulse 20 serving to remove also any prematurely deposited material and thereby exposing a fresh new surface 9 of the substrate for the subsequent deposition stage (Figure 2). Thus a pulsed laser may be used with the equipment of Figure 4 instead of the radiant heat source 30.

In order to bring the substrate 10 to the temperature levels 1 and 3 of Figure 3, other heating means instead of the furnace 26

and susceptor 25 may be used in the apparatus of Figure 4, for example RF induction heating of a susceptor 25 or the provision of resistance heaters within a substrate support (25) inside the reactor vessel 21.

5 Different designs for the reactor vessel 21 may be used, for example as described in GB-A-2 146 663, and gas supply systems as described in GB-A-2 146 663 may be used with these reactor vessels and with the vessel 21 of Figure 4. In a particularly attractive modification the invention is incorporated into a method involving 10 photolytic decomposition of volatile Cd and Te compounds as described in WO-A-86/02951. This permits the use of temperature levels 1 and 3 of Figure 3 in the range of, for example, 220°C to 270°C. The equipment has a lamp or other means for producing the ultra-violet or other light radiation used to decompose the Cd and 15 Te compounds, and a pulsed source of heat radiation to produce one or more heat pulses in accordance with the invention. In this case, the non-oxidising gas flow 5 over the substrate 10 during the application of the heat pulse 20 may comprise the inert gas or gases (for example nitrogen or a noble gas such as helium) used in 20 the deposition stage in accordance with the method of WO-A-86/02951.

It is possible to expose the whole of the upper surface 9' of the substrate 10 to the heat-pulse cleaning treatment or to localise the treatment to particular areas of the substrate 25 surface 9'. When using a radiant heater 30, the heat pulse may be localised by positioning a stencil mask in contact with the surface 9' or by imaging the radiant heat through an optical system with an external mask. In both cases, surface material 8 is only removed where exposed to the radiant heat at localised areas 30 defined by windows in the mask. With a pulsed laser, the heat pulse treatment may be localised by finely focussing the laser beam, for example to an area of 10 or 20 μm diameter and using an x-y steering arrangement to direct the laser so as to pulse only the localised areas of the surface 9' which it is desired to 35 treat. By thus subjecting only localised areas of the substrate

surface 9' to the heat pulse 20, the heating of other areas of the substrate 10 where sensitive circuit elements may be present can be reduced.

Figures 5 to 7 illustrate one example of an embodiment where 5 the structure of the substrate 10 is such as to localise the heat-pulse cleaning of the semiconductor surface and to protect sensitive circuit elements from heating. In this case, the substrate 10 of, for example, monocrystalline silicon has a thick insulating layer structure 53 at its top surface. The structure 53 10 may comprise superimposed layers of insulating material, which in a typical silicon circuit may comprise a bottom layer of silicon dioxide and an uppermost layer of, for example, silicon nitride. Electrically conductive connections 54 of, for example, polycrystalline silicon and/or a refractory metal such as tungsten 15 are embedded in the insulating layer structure 53 and connect regions of circuit elements formed in the substrate 10. Figures 5 to 7 show, by way of example, one such circuit element region 55, for example a source or drain region of a MOS transistor. These circuit elements are located beneath the thick insulating layer 20 structure 53.

Windows 56 are present in the insulating layer structure 53 where it is desired to form cadmium mercury telluride detector elements 61 (see Figure 7) in contact with the silicon surface 9 of the substrate 10. As illustrated in Figure 5 a thin surface oxide 25 layer 8 is present at these windows and is removed as described earlier with reference to Figures 1 and 3, by applying a heat pulse 20 in a non-oxidising gas stream 5. The thick layer structure 53 masks the circuit elements from the heat pulse 20. Thereafter, as described with reference to Figure 2, a layer 11 of 30 cadmium mercury telluride is grown by deposition of material from gas stream 15 (which includes the non-oxidising gas 5). The substrate 10 with its layers is then removed from the reactor vessel 21.

The cadmium mercury telluride layer 11 is crystalline where 35 grown on the clean silicon surface 9, but it may be highly

polycrystalline or even amorphous where deposited on the insulating layer structure 53. Using a photolithographic and etching process, this polycrystalline or amorphous part of the cadmium mercury telluride layer 11 may be removed from the insulating layer
5 structure 53 to leave appropriately shaped islands of crystalline cadmium mercury telluride for the detector elements 61. Contact windows may then be opened in the insulating layer structure 53, and the detector elements 61 may be provided with deposited metal electrodes 64 which connect the detector elements 61 to the circuit
10 connections 54 of the substrate 10.

Although not shown in Figure 6, a CdTe buffer layer 12 may be grown on the clean silicon surface 9 and on the insulating layer structure 53, from the gas stream 15 before depositing the material for the cadmium mercury telluride layer 11. Furthermore after
15 growing the layer 11, a passivating layer, for example of CdTe, may be deposited on the top of the layer 11. When etching the layer 11 to provide the detector element body 61, the corresponding parts of these two CdTe layers are removed except over and under the body parts 61.

20 As already described herein, the invention may be used with vapour-phase deposition systems operating with low gas pressure in the reactor vessel 21. It is also possible to use the heat-pulse cleaning process in equipment designed for molecular beam epitaxy instead of vapour phase epitaxy. In this case a vacuum is present
25 in the reactor vessel, and the heat pulse is applied with the substrate 10 in the non-oxidising ambient provided by the vacuum. The vaporized material 8 is sucked away by the vacuum pump. Then, while maintaining the vacuum, molecular-beam sources which produce gas streams comprising the Hg, Te and Cd reactants are switched on
30 to direct these beams of reactants onto the clean surface 9 of the substrate 10 so as to grow the layers 11 and 12. Alkyls of Cd and Te in a hydrogen carrier gas stream may be used to provide the beams comprising the Cd and Te. In another form an effusion source containing CdTe may be used for the growth of CdTe, and
35 separate effusion sources of Te and Hg may be used for the growth

of HgTe. Except when the heat pulse is applied, the temperature of the substrate 10 may be very low, for example less than 250°C or even less than 220°C for molecular beam growth of the layers 11 and 12.

5 In methods in accordance with the present invention the material may be deposited from a gas stream 15(5) or another vapour phase as crystalline cadmium mercury telluride on the clean substrate surface 9. However, as already described herein, the material may be deposited in one form (for example alternate layers 10 of CdTe and HgTe) and then grown into crystalline cadmium mercury telluride. Thus, in another example, the material may be deposited with a sufficiently low substrate temperature as to be highly polycrystalline or amorphous, and this deposited layer 11 may be annealed subsequently by heating to grow into the desired 15 crystalline cadmium mercury telluride material for the layer 11 which is then used to form the electronic device. This subsequent annealing may be performed either inside or outside the deposition-reactor vessel (21). As hereinbefore described, the first phase of the deposition may comprise a buffer layer 12 of 20 crystalline CdTe. In a further modification in accordance with the invention only the buffer layer 12 of CdTe is grown on the heat-pulse cheaned surface 9 in the reactor vessel (21) from the gas stream 15 (5) or another vapour phase; thereafter the substrate 10 with the CdTe layer 12 is removed from the reactor 25 vessel (21), and the material for the crystalline cadmium mercury telluride layer 11 is deposited and grown in some other manner, for example by liquid-phase epitaxy on the CdTe layer 12.

From reading the present disclosure, other modifications will be apparent to persons skilled in the art. Such modifications may 30 involve other features which are already known for deposition and epitaxial growth and in the manufacture, design and use of electronic devices of cadmium mercury telluride and other materials and which may be used instead of or in addition to features already described herein. Although claims have been formulated in this 35 application to particular combinations of features, it should be

understood that the scope of the disclosure of the present application also includes any novel feature or any novel combination of features disclosed herein either explicitly or implicitly or any generalisation or modification of one or more of those features which would be obvious to persons skilled in the art, whether or not it relates to the same invention as presently claimed in any claim and whether or not it mitigates any or all of the same technical problems as does the present invention. The applicants hereby give notice that new claims may be formulated to such features and/or combinations of such features during the prosecution of the present application or of any further application derived therefrom.

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Claims:

1. A method of manufacturing an electronic device comprising cadmium mercury telluride, in which material comprising mercury, cadmium and tellurium is deposited from a vapour phase onto a surface of a substrate inside a reactor vessel while the surface of the substrate is heated to a temperature below 550°C, a crystalline layer comprising cadmium mercury telluride being grown on the substrate from the deposited material, and in which further device fabrication steps are effected using at least part of the crystalline layer to provide a part of the electronic device, characterised by (a) irradiating the surface of the substrate to apply a heat pulse which removes surface material from the substrate and thereby to leave a clean surface of the substrate suitable for the growth of the crystalline layer, (b) thereafter depositing the material for the crystalline layer on the clean surface, and (c) maintaining the substrate in a non-oxidising ambient in the reactor vessel during steps (a) and (b).

2. A method as claimed in claim 1, further characterised in that the surface of the substrate is heated to above 550°C by the heat pulse, and at least most of the material for the cadmium mercury telluride is deposited when the temperature of the surface of the substrate has fallen to below 550°C.

3. A method as claimed in claim 1 or claim 2, further characterised in that the non-oxidising ambient is provided by a gas which forms part of a gas stream which is passed over the substrate during the deposition.

4. A method as claimed in claim 3, further characterised in that, the non-oxidising gas serves to carry one or more of the mercury, cadmium and tellurium to the substrate during said deposition.

5. A method as claimed in claim 3 or claim 4, further characterised in that the non-oxidising gas is hydrogen, nitrogen or a noble gas.

6. A method as claimed in claim 4 or claim 5, further

characterised in that the mercury is supplied to the gas stream by passing the non-oxidising gas over a heated reservoir of liquid mercury.

7. A method as claimed in anyone of claims 3 to 6, further
5 characterised in that, after the end of the heat pulse, the tellurium is introduced into the gas stream as a volatile tellurium compound.

8. A method as claimed in anyone of claims 3 to 7, further characterised in that, after the temperature of the surface of
10 the substrate heated by the heat pulse has fallen to below 500°C, the cadmium is introduced into the gas stream as a volatile cadmium compound.

9. A method as claimed in anyone of the preceding claims, further characterised in that an intermediate layer of a
15 telluride of either mercury or cadmium is grown on the substrate before the layer of cadmium mercury telluride.

10. A method of manufacturing an electronic device comprising cadmium mercury telluride, in which a gas stream comprising cadmium and tellurium is passed over a substrate
20 inside a reactor vessel while a surface of the substrate is heated so as to deposit a cadmium telluride layer on the substrate, after which an epitaxial crystalline layer of cadmium mercury telluride is grown on the cadmium telluride layer and further device fabrication steps are effected using at least part
25 of the crystalline layer of cadmium mercury telluride to provide a part of the electronic device, characterised by (a) irradiating the surface of the substrate to apply a heat pulse which removes surface material from the substrate and thereby to leave a clean surface of the substrate suitable for the growth of
30 the cadmium telluride layer, (b) thereafter depositing the cadmium telluride layer on the clean surface, and (c) maintaining the substrate in a stream of non-oxidising gas in the reactor vessel during steps (a) and (b).

11. A method as claimed in anyone of the preceding claims,
35 further characterised in that the heat pulse is produced by

switching a radiant heat source directed at said surface of the substrate.

12. A method as claimed in anyone of claims 1 to 10, further characterised in that the heat pulse is produced by a pulsed laser directed at said surface of the substrate.

13. A method as claimed in anyone of the preceding claims, further characterised in that the substrate is of semiconductor material, and that the surface material which is removed by the heat pulse comprises an oxide of the semiconductor substrate material.

14. A method as claimed in claim 13, further characterised in that the substrate is of monocrystalline silicon and the surface of the silicon substrate is heated to above 800°C by the heat pulse.

15. A method as claimed in claim 13, further characterised in that the substrate is of monocrystalline germanium.

16. A method as claimed in anyone of claims 13 to 15, further characterised in that the oxide is removed by the heat pulse from one or more windows in a thick insulating layer structure at the surface of the semiconductor substrate.

17. A method as claimed in anyone of claims 13 to 16, further characterised in that semiconductor circuit elements have been formed in the substrate before applying the heat pulse and before depositing the material for the crystalline layer.

18. A method of manufacturing an electronic device comprising cadmium mercury telluride, substantially as described with reference to Figures 1 and 2, or Figure 3, or Figure 4, or Figures 5 to 6 of the accompanying drawings.

19. An electronic device comprising cadmium mercury telluride, and manufactured by a method claimed in anyone of the preceding claims.

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