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METHOD FOR MULTILAYER SEMICONDUCTOR DEVICE PROCESSING.

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alphabetical order. Can be changed if you like

Abstract of disclosure.

This specification describes a new method of fabricating semiconductor devices which have a thin film sandwich structure. That is, in particular, electrically-alterable read-only semiconductor memory devices which comprise a metal film, then two insulating films on a semiconducting substrate; and photosensitive Schottky barrier diodes which comprise an insulating film, then a metal film on a semiconducting substrate. The multiple thin film formation is achieved in a single processing step by the anodization of a metal-covered semiconductor

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Semiconductor memory elements possessing the sandwich structure shown in fig. 1. (have recently become commercially available[1] and possess attractive features as regards long-information-retention time and electrical alterability. The operation of such a device is described in reference 2. The device is commonly termed a memory of the MNOS or MAOS type, where M

Can delete; do not have to justify why stuff works or not

Prior Art.

refers to the top metal coating, S to the base semiconductor (usually silicon), O to insulator II (usually silicon dioxide) and N or A to insulator I (being respectively silicon nitride or aluminium oxide). The two insulators are commonly formed in separate processing steps e.g. thermal oxidation of ~~Si to~~ silicon to silicon dioxide, followed by either reacting silane with ammonia[3] to form silicon nitride, or pyrolytic deposition[4] of ~~Al_2O_3~~ aluminium oxide from aluminium bromide in a nitric oxide-forming gas mixture. Although the above processes show promise of leading to successful device fabrication the multiple-step nature of the ~~process~~ formations increases the processing time and complexity, and thus the manufacturing cost, besides rendering the device more prone to contamination, with subsequent degradation of electrical properties.

This invention is directed towards a fabrication technique that allows both insulating films to be formed in a single processing step. It involves the use of an electrolyte (gaseous plasma or aqueous solution) to convert, by anodization, a metal film, previously deposited onto a semiconductor wafer, into an insulator whereupon the process is allowed to continue with the result that the underlying semiconductor also commences to be converted to an insulator. This latter insulator grows at the interface between the former insulator and the semiconductor, thus enabling realisation of the required insulator structure in one processing step.

Photosensitive Schottky barrier diodes are of interest in both photogalvanic (detector) and claims = multilayer T.F. devices formed by single anodization step

= A mean to control spectral response of Schottky photodiodes while providing a passivation layer & fine control over metal thickness.

wording excludes uses such as passivation layer formation and restricts substrate to semiconductor

usually broad terms are employed in attempt to cover more ground.

photovoltaic (detector, direct radiation - electricity conversion) applications on account of their acknowledged fast response time and sensitivity to short wavelength (blue and ultraviolet) radiation. A typical structure is shown in fig. 2. The insulating layer serves as both a device encapsulant and an antireflection coating. The metal layer is partially transparent and its interface with the semiconductor yields a metal - semiconductor surface barrier diode (Schottky diode). In all known cases, of which reference 6 is an example, the metal layer is first deposited on the semiconductor and the insulating film, if used at all, is then added without seeking to change the metal film at all. The initial metal film deposition is a critical process step as the thickness of this layer must be very low (< 100 Å) to enable good light transmission to the active region of the diode. Any covering insulating film must then be subsequently deposited without damaging the barrier metal.

This invention is directed towards a fabrication technique that removes the critical nature of the metal deposition step; the barrier metal thickness is subsequently (i.e. after deposition) defined by anodizing in a gaseous plasma or aqueous solution electrolyte. Furthermore, the resulting anodic film forms on top of the metal being ~~anodized~~ ~~thinned~~. thinned and can constitute both an antireflection coating and an encapsulating protective layer.

For both the devices described above a dc low pressure discharge, induced - rf, arc or microwave discharge, as described for example in reference 5, can be utilized for the plasma environment in which the anodization could be carried out. If solution anodization is used, a wide range of electrolytes is available, see for example reference 7. In all cases the arrangement must allow for the insertion of a semiconductor wafer, supporting a previously-deposited metal film, into the electrolyte and provision must be made for biassing the semiconductor with a voltage that is positive with respect to another electrode in the electrolyte. This latter electrode serves only to return the anodization current (and main discharge current in the case of plasma anodization in a dc discharge) to the electrolyte and does not contribute metal species to the growing anodic films.

To illustrate the procedure relevant to this invention consider the sequence shown in fig 3, which depicts the above-mentioned semiconductor slice undergoing anodization in an electrolyte. The semiconductor is taken to be silicon, the metal aluminium and the electrolyte as providing oxygen species. Other semiconductors that form an insulating anodic covering could be used, e.g. germanium or gallium arsenide; other metals that form an insulating anodic covering could be used, e.g tantalum, niobium, vanadium, titanium, zirconium, hafnium, tungsten; gases that support plasmas suited to the anodic conversion of semiconductors and metals to insulators could be used, e.g. oxygen, methane, hydrogen sulphide ; solutions that enable anodic conversion of semiconductors and metals to insulators could be used, e.g. sulphuric acid, phosphonic acid, citric acid etc.

Fig. 3a shows the case of the deposited metal film on the semiconductor surface. ~~which is remote from that surface to while the~~ Fig 3b depicts the situation after the elapse of some period t_1 of anodization, after which part of the metal film is converted to insulator. The anodization of the metal is shown as complete in fig 3c, whereupon further anodization leads to creation of a second insulating layer, see fig 3d.

With reference to the proposed application of this invention to the devices discussed above consider first the semiconductor memory element which could result after elapse of time t_3 (see fig 3d). In devices of this nature it is necessary to have a thin (i.e. ~ 20 Å) bottom insulating layer (e.g. SiO_2 in fig 3), and a thicker (i.e. ~ 1000 Å) top insulating layer (e.g. Al_2O_3 in fig 3). With regard to the present invention the top layer thickness can be predetermined by knowing the deposited metal layer original thickness (D_{Al}) and the relative densities of the metal (ρ_{Al}) and resultant insulator ($\rho_{Al_2O_3}$) viz:

$$D_{Al_2O_3} = D_{Al} \cdot \frac{W_{Al_2O_3}}{2W_{Al}} \cdot \frac{\rho_{Al}}{\rho_{Al_2O_3}}$$

where W refers to molecular or atomic weight. The bottom layer (e.g. Al_2O_3 in fig 3) thickness can be estimated during the period of formation by either in-situ optical measurements, or by monitoring the anodization parameters e.g. the voltage rise on constant current anodization. Because film formation by plasma anodization can be a slow process (typically 5 Å min^{-1}) and slow rates can also be achieved in ~~salt solution~~ dilute solution anodization, good control over the thickness of insulator II can be achieved.

Consider now the photosensitive Schottky barrier diode which ~~could~~ result after elapse of time t_1 (see fig. 2b). The anodization process allows fine control over the barrier metal final thickness. The metal consumed in sectioning from the initial metal thickness to the barrier metal final thickness determines the insulator thickness, as described for the previous example. The spectral response of the diode is affected by the insulator thickness, but not so critically as by the barrier metal thickness. Thus, by the simple expedient of a not-too-critical initial metal deposition the diode's optical characteristics can be finely-controlled by the subsequent anodization process.

The process described in this ~~invention~~ specification is especially useful in that it provides (i) a means of forming the two insulators of a metal-double insulating layer-semiconductor memory device in a single processing step; (ii) a means of forming an antireflection-cum-encapsulating coating on a Schottky barrier diode, simultaneous with controlling the barrier metal thickness, in a single processing step. For ultra-clean conditions the processing step can utilize a gaseous plasma electrolyte and apparatus compatible with high vacuum technology. Alternatively the single anodization step can utilize an aqueous solution electrolyte. In both cases a simple, routine method results and good control is afforded over critical film thicknesses. Furthermore, there is some evidence [8] that plasma-grown oxides are particularly radiation-resistant and thus memory, detector and energy conversion devices produced by the method described in this specification may be attractive for use in intense-radiation environments.

What is claimed is:

1. A procedure for fabricating metal-double insulating layer-semiconductor memory devices in which a metal is deposited onto one side of a semiconductor slice, whereupon the sample is anodized in an electrolyte, which can be a gaseous plasma or aqueous solution, such that firstly the deposited metal is wholly converted to an insulating layer, which is a compound of the metal and some specie of the electrolyte, and then secondly the anodization is allowed to continue thus converting a portion of the underlying semiconductor to an insulator, which is a compound of the semiconductor and some specie of the electrolyte.

2. A procedure for fabricating insulator-metal-semiconductor photosensitive diodes in which a metal is deposited onto one side of a semiconductor slice, whereupon the sample is anodized in an electrolyte, which can be a gaseous plasma or aqueous solution, such that the deposited metal is partially converted to an

insulating layer, which is a compound of the metal and some specie of the electrolyte.

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