Apparatus and method for thin film deposition especially in reactive conditions. The most important problem solved by the invention is the realization of optical coatings with negligible optical absorption, of high quality and low cost even on unheated substrates, being the improvement due to the introduction of a further plasma at RF/pulsed DC, in comparison with the previous techniques, produced by the substrates holder RD/pulsed DC bias which generates a plasma in front of the substrates. The invention lies in the technical field of the thin film treatments and in the application field of the production of thick films, in particular for optical use. This further plasma allows obtaining the right stoichiometry of the deposited film by increasing the reactivity of the reactive gas present in the plasma and, in addition, introduces an energetic ion bombardment of the substrate before and during the growth of the film which improves the adherence and the deposit compactness.
APPARATUS FOR THIN FILM DEPOSITION, ESPECIALLY UNDER REACTIVE CONDITIONS

SUMMARY OF THE INVENTION

[0010] These objects can be attained, in accordance with the invention, in a method which comprises the steps of:

[0011] (a) mounting a substrate to be coated on a crucible holder in an evacuable chamber and so that the substrate is spacedly juxtaposed with a crucible containing a component of a coating to be applied to the substrate;

[0012] (b) evacuating the chamber;

[0013] (c) positioning a shutter between the crucible and the substrate and heating the component in the crucible with a high energy beam;

[0014] (d) admitting a gas mixture to the chamber;

[0015] (e) connecting the substrate holder to a radio frequency or pulsed direct current source so that the substrate holder is poled cathodic and a plasma is formed at least around the substrate to create a self bias of several hundreds of volts on the substrate holder and a surface of the substrate is bombarded with particles from the plasma;

[0016] (f) withdrawing the shutter from its position between the crucible and the substrate, bombarding the component with low energy electrons to ionize the component at least in part and depositing the component and the at least one gas on the substrate; and

[0017] (g) controlling the ionization of the component so that the self bias is reduced by at least 50%.

[0018] Advantageously, the coating is carried out in a reactive mode, i.e. with the ionized components reacting with at least one gas in the gas mixture. The coatings which can be deposited can be oxides, nitrides, oxy-nitrides and carbides of substantially any component, usually a metal which can be melted and ionized in the crucible, including aluminum, tin, silver and chromium. Elemental metals may be deposited without reaction, for example, gold.

[0019] The apparatus which is used can comprise:

[0020] a vacuum chamber connectable to a pump adapted to evacuate the chamber;

[0021] at least one crucible in the chamber;

[0022] a substrate holder in the chamber receiving a substrate to be coated and juxtaposed with the crucible;

[0023] a mechanical shutter in the chamber interposable between the crucible and the substrate;

[0024] a high-energy source for heating a component of a coating to be deposited upon the substrate in the crucible;

[0025] a radio frequency or pulsed direct current source connectable to the substrate holder for producing a plasma around the substrate and imparting a self-bias to the substrate holder poling the substrate holder cathodic;

[0026] means for feeding a gas mixture to the chamber including at least one gas reactive with the component to form a coating on the substrate; and
[0027] A low energy electron source for ionizing the component to reduce the self-bias and deposit a reaction product of the component and the at least one gas on the substrate, the shutter being movable from one the crucible and the substrate to permit ionization of the component.

[0028] The invention utilizes the plasma generated around the substrate and at the substrate holder by the radio frequency or pulsed direct current source connected to the cathodically poled substrate holder to produce a self-bias around and in front of the substrate or substrates which can vary from several tons of volts to many hundreds of volts and usually is at least several hundred volts. The gas which is used can include an inert gas like argon and reactive gases like oxygen and nitrogen or mixtures thereof and the plasma may be maintained at a pressure in the chamber of $10^{-3}$ to $10^{-2}$ Torr. The chamber is initially evacuated to about say $10^{-4}$ Torr before the gas mixture is admitted to the chamber.

[0029] The effects of the plasma are manifold and include:

[0030] ion bombardment from the plasma of the substrate surface usually by reactive gas molecules which appears to activate the surface and promote bonding of the thin film coating and mechanical integrity of the latter. The plasma also contributes to ionization and excitation of the reactive gas which tends to drive the reaction in the direction of formation of the reaction products and compensates for possible dissociation caused by energetic ion bombardment.

[0031] In addition, the plasma appears to bring about an ion bombardment of the growing film and hence a higher film compactness during its growth with a consequent improvement in adherence of the film to the substrate.

[0032] The plasma also contributes to an increase in the duration of the “adatom” phase which also results in an increase in compactness and mechanical stability of the film and a refractive index value which is close to that of the bulk material.

[0033] Finally it has been found, most surprisingly, that the presence of the plasma, coupled with the dramatic decrease in the self-bias brought about by ionization of the coating components, results in an increase in the maximum deposition rate without significant absorption so that the duration of the process can be reduced along with the processing cost.

[0034] The apparatus of the invention permits optical coatings to be applied to substrates without noticeable absorption of the film and a significant increase in the refractive index by comparison with the reactive indices of coatings applied with other apparatus even at higher deposition rates.

BRIEF DESCRIPTION OF THE DRAWING

[0035] The above and other objects, features, and advantages will become more readily apparent from the following description, reference being made to the accompanying drawing in which:

[0036] FIG. 1 is an axial section of a prior at arrangement;

[0037] FIG. 2 is an axial section of an apparatus according to the invention; and

[0038] FIG. 3 is a detail of a modification of the apparatus of FIG. 2.

SPECIFIC DESCRIPTION

[0039] The prior art apparatus shown in FIG. 1 comprises a vacuum chamber 6 which has a fitting 6a at one end connected to a low-energy electron generator 1. Within the chamber 6, which can be connected by a fitting 5 to a suction beam arrangement capable of reducing the pressure in the vacuum chamber 2, say $10^{-5}$ Torr, there is provided a high-energy electron generator 2 which can be an electron beam gun. A current source 9 is connected between the crucible holder 10 and the low-energy electron generator 1. Fittings 11 are provided to introduce process gas into the chamber and a substrate holder 4 is mounted on a shaft 7 extending through an insulator 8. As has been described previously, the workpiece may be provided on the substrate and is exposed to ions evaporated from the material 3a in the crucible 3 on the holder 10. The chamber 6 is evacuated and electron beam vaporization of the material 3a causes that material to react with the reactive component of the process gas introduced at 11 for deposition on the workpiece.

[0040] In FIG. 2, corresponding reference numerals have been used to represent elements in the system of FIG. 2 which are similar to those of FIG. 1. The chamber 6 here, connected to the suction beam 20 via the vacuum gauge 21, also has a process gas inlet 22 connected to the process gas source 23 by a valve 24, a flow meter 25 and a pressure gauge 26.

[0041] A similar process gas source 27 has a valve 28, a flow meter 29 and a pressure gauge 30 connecting it to the process gas inlets 11 which discharge at the mouth of the crucible 3.

[0042] The crucible holder 10 is rotatable by a motor 31 and the feed-through 7 in the insulator 8 is likewise rotatable, e.g. by a motor 32. The radio frequency source has been illustrated in FIG. 2 at 13 and is connected by the matching network 12 to the feed-through 7. The substrates 14 on the holder are blanketed in a plasma which has been represented at 15 and a monitor 19 is provided to measure the thickness of the coating on the substrate. A mechanical shutter 18 can be swung and represented by the double-headed arrow 33 so that in one position it covers the mouth of the crucible 3 and in another position is swung away from that mouth to allow vaporized material from the crucible to pass through the plasma 15 and deposit on the surface of the substrates 14 which may be lenses or the like to be coated with, for example, a tin oxide coating.

[0043] In the method of the invention, the substrates 14 are mounted on the rotatable holder 4 and after chemical cleaning externally are activated or further cleaned by plasma 15. The rotation of the substrate holder 7 ensures thickness uniformity and thin films on the substrate. While the substrate holder is shown in a horizontal orientation it could, of course, be vertically oriented as well.

[0044] Chamber 6 is evacuated through the fitting 5 via the suction pump 20 to a pressure of about $10^{-6}$ Torr. While the shutter is positioned in front of the source of coating ions as shown at 3, the metal 3a within the crucible is heated, e.g. by heating of the crucible electrically, and by the high-energy electron beam from the source 2, thereby melting the material to be vaporized.
The gaseous mixture, e.g. argon and at least one reactive gas, for example nitrogen or oxygen, is admitted through fitting 11 and the gas flow is controlled by the vacuum gauges and flow meters. One of the sources 23 or 27 may be provided with the reactive gas while the admitted argon or mixtures of argon and the reactive gas may be prepared and admitted through the same inlets.

The radio frequency source 13 is activated thereby generating the plasma 15 whose particles bombard the substrates 14 and further activate or "clean" the surfaces thereof. The self-bias of hundreds of volts is developed on the substrate holder.

In FIG. 3 crucible holder 40 has been shown and has crucibles 41 and 42 containing different materials 43, 44 which can be evaporated and the shutter 18 can cover the one in the active position. By rotation of the holder 40, the different crucibles can be brought into position. Multiple electron beam sources can be used as shown at 45 and 46 and can be selectively connected at 47 to the voltage source 48.

We claim:

1. An apparatus for applying a thin film coating to a substrate comprising:
   a vacuum chamber connectable to a pump adapted to evacuate said chamber;
   at least one crucible in said chamber;
   a substrate holder in said chamber receiving a substrate to be coated and juxtaposed with said crucible;
   a mechanical shutter in said chamber interposable between said crucible and said substrate;
   a high-energy source for heating a component of a coating to be deposited upon said substrate in said crucible;
   a radio frequency or pulsed direct current source connectable to said substrate holder for producing a plasma around said substrate and imparting a self-bias to said substrate holder poling said substrate holder cathodic;
   means for feeding a gas mixture to said chamber including at least one gas reactive with said component to form a coating on said substrate; and
   a low energy electron source for ionizing said component to reduce said self-bias and deposit a reaction product of said component and said at least one gas on said substrate, said shutter being movable from one said crucible and said substrate to permit ionization of said component.

2. The apparatus defined in claim 1 wherein said substrate holder is mounted for rotation in said chamber.

3. The apparatus defined in claim 2 wherein said chamber is formed with an insulated feed-through for connecting said source to said substrate holder.

4. The apparatus defined in claim 3, further comprising an instrument for measuring the thickness of said coating on said substrate for controlling the deposition of said reaction product on said substrate.

5. The apparatus defined in claim 4 wherein said crucible is electrically heated.

6. The apparatus defined in claim 4 wherein said component is heated in said crucible by sputtering.

7. The apparatus defined in claim 4 wherein said source is a radio frequency source.

8. The apparatus defined in claim 4 wherein said crucible is rotatable in said chamber.

9. The apparatus defined in claim 4, further comprising another crucible containing a respective component capable of forming a reaction product which can be deposited on said coating.

10. The apparatus defined in claim 4 wherein said component is heated in part by an electron beam gun.

11. The apparatus defined in claim 10, further comprising another electron beam gun in said chamber for heating said component.

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