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Patent application**W. C. Heraeus GmbH & Co. KG****Method for the manufacture of a metal oxide powder or a semiconductor oxide powder, an oxide powder, a solid and its application**

The invention relates to a method for the manufacture of a metal oxide powder or a semiconductor oxide powder. The invention further relates to an oxide powder, a solid manufactured therefrom and its application.

A main field of application of the present invention is the ITO or indium-tin-oxide, which is a transparent and electrically conducting ceramic material. This particular property permits quite a few applications, such as the separation of thin films for liquid crystal or plasma displays, electromagnetic shielding, heating devices or other systems, in the most cases on glass or plastic. An important case of application is cathode sputtering on glass, which requires as high an electric conductivity as possible and which is followed by an etching cycle. In cathode sputtering, more or less big parts of the target material are removed by ionic bombardment and deposited on a substrate. That is the reason why the properties of the deposition layer on a substrate depend on the properties of the target, though not exclusively, but to a large extent.

ITO is a semiconductor that has the property of being transparent over a wide wavelength range. Its high conductivity is based on a high concentration of charge carriers with a high mobility. The conductivity is equal to the product from the number and the mobility of the charge carriers:

$$C = N \times M$$

ITO is an indium oxide (In_2O_3) that is doped with tin atoms. In this process, certain indium atoms belonging to the third group of the periodic table of the elements are replaced by tin atoms belonging to the fourth group of said table. This results in an excess of electrons and, thus, of charge. Charge carriers are the electrons which, owing to the tin atoms (Sn atoms) and the oxygen vacancies, are present in excess. Both their concentrations are of the same characteristic magnitude of particles with a low conductivity, that is

$$\text{Sn}^* = \text{V}_\text{o} = 3 \times 10^{20} \text{ cm}^{-3}$$

Unfortunately, only a small part of these electrons is mobile, because of an unfavorable structure. The mobility is measured by means of the Hall effect which is based on a deflection of the field lines of a current-carrying conductor through a magnetic field. The mobility is reduced by structural defects of the crystal lattice.

Other oxide or non-oxide ceramics, for example nitrides, and in particular aluminium nitride, which do not have the interesting particular transparency property, may nevertheless be electrically conducting under certain conditions or have other interesting features, this also finding use as will still be disclosed below. Apart from the fineness and the properties of nanomaterials, it is particularly known that thermal conductivity is, in general, correlated with electric conductivity.

According to the state of the art, most of the target materials for cathode sputtering, various parts, granulates, and powder are manufactured today by mixing indium oxide and tin oxide powders according to wet-chemical procedures. These powders are mixed at variable ratios, wherein a weight mixing ratio of 90% indium oxide to 10% tin oxide is used in the most cases. The mixture will be more homogeneous if the hydroxides are mixed and subsequently dried.

Thereafter, this powder is compacted by sintering, hot isostatic pressing (commonly known as HIP), hot pressing or by means of a different, but similar method. In this context, reference should be made to the diagram in Fig. 1 from the document by H. Enoki,

E. Echigoya and H. Suto, "The intermediate compound in the In_2O_3 - SnO_2 system", in the Journal of Materials Science (2651991), 4110-4115. It can be seen therefrom that the two phases are at the edges of the diagram – the C1 and T zones of Fig. 1 – and that the desired zone that is represented by the vertical dotted line is the zone where the tin oxide is in the mixed crystal in the indium oxide, hence in the C1 zone where the temperature is close to 1200 °C. The diagram should not be seen as a constitution diagram resulting from reversible cooling; all the same, the diagram reveals that the desired product results from a diffusion into the solid state, which is intricate and requires much special knowledge from persons who are familiar with this subject matter. The C1 zone would consist of $(\text{In},\text{Sn})_2\text{O}_3$ and the C2 zone of $(\text{In}_{0.6}\text{-Sn}_{0.4})_2\text{O}_3$.

At a ratio of 90 to 10, as it is represented by the dotted line in Fig. 1, it can be seen that tin oxide SnO_2 precipitates slowly and at a low temperature, with this precipitation becoming stronger above 1000 °C.

The method according to patent FR 94874 yields a completely different ITO. The manufacturing procedure is the subject of patent FR 94874. The results, that is the properties of the manufactured powder, are described in detail in patent EP 0 879 791 B1.

The metal alloy is melted at a ratio of amount of substance that permits, after oxidation, to achieve the desired oxygen value of, for example, 89.69 w/w percent indium and 10.31 w/w percent tin, corresponding to 36 atom % indium, 4 atom % tin and 60 atom % oxygen, resulting in a weight ratio of 90 to 10 (indium oxide to tin oxide). The liquid is completely homogeneous and extends in a plasma that consists, preferably, of pure oxygen in the form of a calibrated jet which is a few millimeters in diameter. The oxygen reaction sets in at a very high temperature in an environment with a very high enthalpy. Oxidation takes place at the very finely sputtered alloy. In concrete terms, the plasma consists of O_2 , O_2^+ , O^{2+} , O , O^+ , In , In^+ , Sn , and Sn^+ particles at ratios of amount of substance that depend on the enthalpy and are difficult to determine. The oxide is a mixed oxide, that is an oxide whose crystal lattice has a triperiodic structure, where the indium, tin and oxygen atoms are distributed over positions that are arranged in the vicinity of

those positions that can be predicted according to Morse's law, which specifies the equilibrium between the potentials of attraction and repulsion of the two atoms. The velocity of ejection from the plasma nozzle is in the supersonic region. Moreover, the natural cooling rate outside of the exothermic reaction is 10^4 K/sec. Hence, a complete oxidation takes 2 to 3 seconds at this reaction rate.

The reaction time specified may be very short for two reasons. The first reason is a quenching process during the flight, if the heat balance of the reaction in a grain is negative, i.e. if the heat of combustion fails to equalize the cooling process. The second reason is the contact with solids, mainly with the walls of the reaction chamber. In either case and even if the powder continues to be burning in the agglomerates, the theoretical structure fails to be reached. The grains have a mean diameter of 1 to 20 μm . Nevertheless, they agglomerate with each other at the slightest touch.

The compaction of the powder to form solids that are, in the most cases, presently provided for the manufacture of targets for cathode sputtering is achieved by a classical combination of cold and hot pressing or by unidirectional hot pressing or hot isostatic pressing (HIP). In all cases, the heating temperature exceeds 900 $^{\circ}\text{C}$. In patent DE 44 27 060 C1, a temperature of over 800 $^{\circ}\text{C}$ is claimed for powders of 2 μm and 20 μm .

Moreover, US 5,580,641 describes the application of ion implantation of O^+ ions to reduce the number of charge carriers. Conversely, the implantation of hydrogen ions is treated in "Studies of H_2^+ implantation into indium tin film oxides" in "Nuclear instrumentation methods", vol. 37.37, p. 732 (1989). The method of ion implantation is common knowledge.

The method known from US 4,689,075 is a static one. A specific amount of a granulate mixture or tablets is placed on an anvil and removed at a high temperature by means of a plasma torch that is apparently similar to those available on the market for cutting and welding purposes. Such torches consist of a stationary tungsten electrode that is surrounded by a number of gas jets.

It seems that the two components, which are subjected to an intense thermal motion, evaporate at the same time and that the vapors can be caught by being sucked in, whereby a high-quality mixture is formed – as claimed. Conversely, our method does not contain any mixture and is not based on thermal motion.

The method according to the patent mentioned is a static one and operates batchwise, although a more or less automatic charging is also conceivable for its industrial applicability, this resulting in the processing of successive batches.

US patent 4,889,665 follows the aforementioned patent. It claims the use of a plasma torch for heating an amount of granulate or compacted sintered parts.

US patent 6,030,507 describes the production of coarser powders with grain sizes of 1 to 20 μm .

US patent 5,876,683 describes a different technique. Concretely, it is based on the chemical combustion of an organic precursor in a flame. The precursor mentioned is already a metal compound. For example, silazanes, butoxides ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2^-$), acetyl ($\text{CH}_3\text{COCH}_2^-$), or acetonates are disclosed.

The invention aims at improving the state of the art and at specifying an appropriate method, an oxide powder and a solid as well as the latter's application.

This problem is solved by the invention by the independent claims. Advantageous embodiments can be found in the subordinate claims.

The method is a dynamic and continuous one. The constituents are present in the fluid state. The first constituent of the reaction, metal, alloy, mixture, flows in the fluid state or, equivalently, in continuous form. It assumes two roles. On the one hand, it is one of the constituents of the reaction and can be found in the plasma. For example, an analysis of the plasma will identify electrons, ions from the gases – whether oxygen, nitrogen,

argon, hydrogen – and bismuth, indium, tin ions. On the other hand, it also assumes the role of a tungsten electrode which would, however, melt down and become smaller to an unlimited extent.

The complex method comprises four phases:

Phase 1

The plasma is only a part of the method according to the invention. The plasma certainly represents an important preparation phase. In the plasma, the reaction sets in under ideal thermodynamic conditions. Both enthalpy and entropy are positive to a high degree. What is more, the thermal motion of the atoms and molecules is a factor of improvement.

Phase 2

Although new in concept, the plasma itself would not allow serial production. In the method according to the invention, the plasma is sucked in by a strong dynamic negative pressure in a burning point or a combustion chamber of reduced dimensions. It should be noted that the plasma is a mixture that consists of molecules, molecules with dissociated atoms, molecules with ionized gases, ionized atoms, metallic vapors and electrons. This mixture is sucked off as it is formed in the combustion chamber.

Phase 3

The third phase is the sputtering phase. The mixture formed by the plasma is accelerated by a convergent-divergent nozzle to a high velocity that is a multiple of the sound velocity. This acceleration disperses the constituents at a small and well-defined angle into a more or less unlimited volume. A production of 100 kg/hour that is blown at by a jet of 500 m/sec is dispersed at a rate of 55 mg per meter. Since the jet is designed such that it widens as it decelerates, this dilution rate is preserved until cooling is completed, thus preventing the formation of satellites and agglomeration.

Phase 4

The fourth phase is the transport phase. The reaction initiated in the preceding phases is continued and ends under controlled thermodynamic conditions, with an interstice between the forming grains being kept, so that these grains may undergo their individual development without coming into contact with other grains or with the walls. This permits to develop and maintain the nanostructure that has been initiated by the plasma.

Studies of various materials have shown that the method according to the invention permits the continuous production and not the batch production of powders from compounds complying with the definition of nanopowders.

By introducing the basic materials of the continuous reaction into the plasma (plasma bubble with a volume of 1 to 3 cm³), for example the liquid In-Sn alloy, on the one hand and, separately, pure oxygen on the other hand, it is not a mixture that is obtained, but a compound.

The nanograins may tend to gather under the effect of various factors. These factors are moisture, static electricity and various surface parameters that are correlated with their dimensions of a magnitude of some atomic diameters as well as with their extreme surface-to-mass ratio. Actually, these forces are weak interactive forces, but they may have a considerable influence because of the large specific surface of the nanopowder.

Under these conditions, it may be considered that these surface forces provide grain agglomerates, which may even reach the submicron range, with a certain strength that may, however, break apart because of a low moisture content or a certain ultrasonic excitation.

Under these conditions that are measured with a modern laser granulometer, the following must be put forward after an ultrasonic dispersion for a duration of approximately

2 minutes: d_{50} by weight $< 0.50 \mu\text{m}$. This means that 50% of the weight-related amount of substance has a grain size of less than $0.50 \mu\text{m}$.

It must be noted that, reasonably, the interruption or prolongation of phase 4 permits a total or a partial reaction, and this with an entirely new degree of precision.

The invention will be described in an illustrative manner by means of figures in which:

- Fig. 1 shows an indium oxide/tin oxide phase diagram;
- Fig. 2 shows a plasma temperature enthalpy diagram;
- Fig. 3 shows a temperature spectrum;
- Fig. 4 shows a diagram of specific surface/grain size;
- Fig. 5 shows defects according to Frenkel (left) and Schottky (right);
- Fig. 6a shows a foreign atom that replaces an atom (a) or occupies an interstitial position (b);
- Fig. 6b shows an edge displacement perpendicular to the level of the drawing;
- Fig. 6c shows a screw displacement.

The method according to the invention proceeds from the principle that the plasma only provides the possibility of discussing the diagram according to Fig. 1. The likewise fine mixing method, i.e. the procedure that is carried out on the level of hydroxides, is not covered by the diagram.

The oxygen plasma method starts the reaction at a temperature of a magnitude of $10,000^\circ\text{C}$. Fig. 2 shows the plasma temperature as a function of the enthalpy of the system. The oxidation reaction takes place on the spot and is exothermic. In contrast, a zone of a cold atomization gas surrounding the plasma forms behind the nozzle accomplishing the flow and the sputtering. The following table reflects the properties of the jet for a standard nozzle. These values have been verified in experiments.

Values	Input	Output
Pressure [bar]	7	0.95

Temperature [K]	293	165
Mach number	0	1.96
Velocity [m/sec]	0	483

The liquid metal jet flows at a velocity of approx. 3 m/sec into an outlet tube, 2.5 mm in diameter, under a metallostatic column of 500 mm (height of the liquid metal above the outlet).

The plasma is sucked in at a velocity that is below that of the atomization gas.

In view of the as-defined fineness of the plasma components, the mixture can be considered to be homogeneous.

Fig. 3 shows the calculated temperature spectrum that has been verified by laser measurement. The liquid alloy jet with a temperature of, for example, 670 K is identified by the axis 1 of the cast jet, the plasma cone (plasma bubble) with 10,000 K is identified by 2, and the oxygen with 1.96 Mach and 165 K through the zone of the cold atomization gas surrounding the plasma is identified by 3. The area 4 is the reaction and cool-down zone where a homogeneous environment can be assumed and where cooling-down is achieved according to a cubic law.

In particular, the method according to the invention consists in that it provides the forming ITO particles with a free flight path according to the time required for the complete reaction and then controls the cooling phase. Calculations and experiments have shown that, at a velocity of ejection from the nozzle of approximately 480 m/sec and with the relation among the velocities that follow a cubic correlation, i.e. a power of $1/3$ of the path, a free flight path of a magnitude of at least 5 meters is required. The reaction must be completed in the flight section where the plasma is the determinant, that is above 1000 °C. For that reason, this range or this section of the flight path must have the appropriate length of approximately 2 to 3 meters. Subsequently, the generated structure must be maintained in order to avoid separations, in particular of tin oxide. In this manner, a powder consisting of grains of nanometer magnitude is obtained. Their mean di-

ameter is less than $1/100 \mu\text{m}$, hence some ten Angstrom units. The powder manufactured in this manner has an extremely large specific surface. Fig. 4 shows the behavior of the specific surface of a spheroidal powder in relation to the grain size.

As a result, the surface energy of the powder is far above that of the powder manufactured according to the previous method. The surface of the nanopowder is much larger, and the behavior of the surface energy is proportional thereto.

In addition, the characteristic state of the powder shows itself in the diagram (Fig. 1) on the abscissa at 10% and on the ordinate at a very high temperature and, thus, far beyond the sketch. The analysis shows that the tin is in solid solution and has a structure that complies with the C1 zone. The diagram relates to an equilibrium state, and one can see that the atoms are very far from their minimum energy state which they should assume according to the maximum flow theorem.

Once the powder has finally cooled down in a natural manner until completion of the reaction and at a faster rate thereafter and is still present as nanopowder, there are no obstacles to the displacement of particles in the lattice.

It should be noted that the nanopowder is not amorphous.

In practice, the state of the nanopowder corresponds to the absence of identifiable powder grains. Examinations with the scanning electron microscope show ever finer grains while the magnification is increased.

This results in an absence of any and all structural defects. It can be considered to be proved that the defects are the cause of the low electric mobility. This is adequately shown by the fact that the electric conductivity of the depositions achieved by cathode sputtering increases by annealing as well as by the fact that, in the most cases, the ion implantation has reduced the conductivity proportional to the number of defects it caused. The most damaging defects are forming at the grain boundaries of the powder. The grain boundaries represent an interruption in the crystal lattice. This interruption

has different orientations and contains all contaminants that the hot surface has taken up from the atmosphere or by contact. While compaction is in progress, contaminants, such as carbon, are often displaced from the nucleus towards the periphery. The defect is eliminated by the absence of measurable grains and the absence of any contact. The use of oxygen or clean gases prevents the takeup of contaminants during flight.

The microscopic contaminants must be attributed to the difference between the cooling rate and that rate that would be allowed by the formation of a crystal lattice, i.e. the time and the thermodynamic conditions required to ensure that each atom can assume its position.

There are three types of defects. Defects at atom positions are often called thermodynamic defects, because their presence in the crystals is often connected with high temperatures. These are Schottky defects if an atom is caused to leave its equilibrium position and Frenkel defects if a small cation likewise leaves its equilibrium position and migrates to an interstitial position. The Frenkel and Schottky defects are shown in Fig. 5. As far as ITO is concerned, the defects in the type of the atoms are of a structural nature, because the tin, together with the indium oxide, must be in solid solution. The foreign atom either takes the place of a crystal lattice atom or it occupies an interstitial position.

The following table specifies the metallic and ionic radiuses of the three elements that are treated here.

O^{2-}	In	In^{3+}	Sn	Sn^{4+}
1.32	1.66	0.92	1.58	0.74

This gives rise to the assumption that the tin atom may also occupy an interstitial position.

The defects and displacements are develop during the cooling phase. They are, above all, unavoidable whenever atoms have assumed interstitial positions, but they can be

limited by a cooling process that is carried out at a slow rate and in a controlled manner. The three main types mentioned are the subject of Figs. 6a–6c.

As can be concluded from the principle described above, the oxidation reaction is spontaneously started by the very high enthalpy and the state of the plasma. The reaction rate is also high. For example, the entire oxidation reaction can be completed within 5 seconds, although the ITO powder can burn stoichiometrically in the air for 20 minutes. As a consequence, the behavior of the reaction can be completed by quenching at the end of a specified path at a degree of oxidation of 50, 60 and 90%. Thereafter, the cooling rate can and must be checked to ensure that the resulting crystal lattice will be as free from defects as possible. The cooling stage mentioned may be inadequate, either because of a negative heat balance or because of a contact with the wall of the reaction vessel. The first effect can be compensated by preheating or cooling the atomization gas, the second one by an appropriate routing of the gas flow in the reaction vessel. This can be properly achieved by an off-center injection of a suitable form and with the appropriate dimensions. Conversely, it must be noted that the sub-stoichiometric manufacture of oxides, that are useful owing to their conductivity, can be achieved in an economical manner by gas quenching or by other mechanical devices on an exact path. To cool the jet abruptly from that point where it reaches an exact temperature, a probe defining the corresponding path was positioned, and a cooling gas injection was used the effect of which is based on routing and dilution. It should be noted that air with a temperature of 20 °C, whose pressure is reduced from 5 bar to 1 bar, is emitted with a temperature of –88 °C; the emission temperature of argon is –120 °C.

The aforementioned 90/10-ITO powder has been manufactured according to the inventive method. It has the following properties:

Primary particle size	nanosstructure less than 0.10 μm
Powder density	0.69 g/cm^3
Relative density	approx. 10% of the theoretical density
Resistivity (compacted)	10^{-2} ohms-cm or less

The powder is heavy, is not suspended in air, and has an extremely excellent compaction behavior. It compacts as early as at a low pressure of some kg/cm^2 .

To compact the powder mentioned, two method families can be utilized that are well-known to persons familiar with the subject matter. The manufacturing procedures using variants of the classical compaction and sintering method, particularly by pressing at ambient temperature after heating up to a high temperature, are modified as follows: The low-pressure compaction yields a higher density and strength, or the density obtained with the same pressure is higher and can exceed 80% of the theoretical density. Subsequently, the temperature in the present embodiment can be reduced from 800 °C to at least 600 °C or 650 °C.

In the manufacturing procedures where use is made of variants of the hot pressing method, the temperatures are reduced in the same manner. These hot pressing processes can be implemented on hydraulic or mechanical presses, by hot isostatic pressing (HIP) or in a like manner. Irrespective of whether these pressing processes are preceded by a cold compaction process or not, the pressures/densities are improved, as is the case with the aforementioned compaction and sintering method.

The method has been tested and qualified for the oxidation of bismuth, zinc, silicon, and other elements under the conditions described above. Even aluminium nitride nanopowder can, in this manner, be manufactured in a nitrogen plasma. There are four main benefits. First, the cost as compared with the classical methods is low, mainly because of the low energy requirements that must be attributed to the practically complete progress of the reaction itself; second, harmful substances and waste material are not incurred; third, the nanostructure permits an unsurpassed efficiency or fineness; and finally, a reaction can be achieved under controlled stoichiometry. Over and above this, the yield is very close to 100%, because the entire powder can be directly used, without having to be sorted out, comminuted or treated in any other way.

The method according to the invention is applied as follows: An indium and tin batch is weighed at the ratios calculated, so that the desired oxygen content is developing in the

subsequent reaction. The constituents are melted and then introduced into the air or oxygen plasma in the form of a jet of a Newtonian fluid (jet in free fall). The plasma that comprises molecules, ions and atoms (O^{2+} , O^+ , O_2 , O , In , In^+ , Sn , and Sn^+) as well as electrons is blown at by a supersonic nozzle. Contrary to the basic methods mentioned above, the free flight path is very long. It is about 5 meters for ITO.

The powder is collected when it is cold and is filled into an evacuated and sealed container. Subsequently, the container is subjected to a hot pressing process or a cold pressing process, which is followed by a sintering process. Pressing can be carried out unidirectionally on a press or isostatically in a HIP safety housing. Since it was used in the nanopowder state, the powder must be treated at a temperature of a magnitude of only 650 °C instead of temperatures between 900 °C and 1150 °C according to the methods mentioned.

The method according to the invention was also applied to other materials but under the same conditions. Here, reference should be made to bismuth, tin and zinc oxides that were sputtered directly in an oxygen plasma.

The method was used for the industrial production of aluminium of a particular quality as well as of aluminium nitride, with the latter being produced in a nitrogen plasma. The sub-stoichiometric oxide of silicon (SiO) was manufactured with a shorter free flight path. An example of an industrial application will be described below.

A 70-kg batch of an indium-tin alloy with a weight ratio of 89.69 to 10.30 percent is melted at 400 °C. The liquid flows through a calibrated ceramic nozzle, that is 2.5 mm in diameter, in the form of a Newtonian fluid jet. It enters a pure oxygen plasma and is blown at by a supersonic nozzle. The form and diameter of the stainless-steel chamber are selected such that they do not have any effect on the path of the powder. The free flight path is 5 meters. The nozzle is positioned such that the powder follows a kidney-shaped path, before it is sucked in outside of the vessel. The powder is collected in an absolute filter. Its mean diameter cannot be measured, but seems to be within a magnitude of some ten Angstrom units, when observed under the electron microscope.

The powder is filled into an evacuated and sealed container. This container is accommodated in a hot-isostatic-pressing housing where it is exposed to a temperature cycle of 650 °C at 1400 bar for a duration of 2 hours.

After having been removed from the mold, the workpiece has solidified and can be treated easily. Its density is over 99%.

A second industrial application example is as follows: A 500-kg batch of bismuth is filled into a melting crucible. Considering the oxidation tendency of liquid bismuth, the surface should, preferably, be protected. Since bismuth, when cooling down, expands but does not attack steel, the melting crucible consists of steel. Once the metal has reached a temperature that is 150 °C above its melting temperature, the stopper rod is pulled up. The plasma forms as soon as the jet acts as electrode. The hourly throughput is 540 kg for a jet with a diameter of 2.5 mm and 500 mm material to be melted. The powder is collected as described above. The same production with use being made of zinc under the same conditions yields a throughput of 395 kg per hour. The same production with use being made of antimony yields a production volume of 366 kg per hour. In contrast, silicon was introduced into the plasma as powder in the form of a Newtonian fluid jet, with the plasma being charged via a helical conveyor.

Claims

1. Method for the manufacture of a metal oxide powder or a semiconductor oxide powder, characterized in that it comprises a dynamic, continuous and direct oxidation of the metal or semiconductor material that assumes the function of a melt-down electrode in an oxygen plasma, wherein the time of flight of the developing oxygen particles is appropriate for the complete oxidation reaction and without any mechanical contact before having cooled down completely, and wherein the oxidation process is followed by a controlled cooling phase.
2. Method according to claim 1, characterized in that it comprises a compaction phase by sintering or a hot pressing process at a temperature between 550 °C and 800 °C, in particular between 600 °C and 700 °C.
3. Oxide powder, characterized in that it is a nanopowder with a grain size of less than 0.5 μm , with the grains of the nanopowder comprising crystallites that are smaller than 100 nm.
4. Oxide powder according to claim 3, characterized in that it is manufactured in accordance with a method according to claim 1 or 2.
5. Oxide powder according to claim 3 or 4, characterized in that it is formed of at least one material from the indium-tin-oxide, tin oxide, bismuth oxide, zinc oxide, silicon oxide, antimony oxide group.
6. Oxide powder according to claim 5, characterized in that the silicon oxide is sub-stoichiometric.
7. Solid composed of an oxide powder according to one of the claims 3 through 6, characterized in that it has a density of 99% of the theoretical density or a higher density.

8. Solid according to claim 7, characterized in that it is manufactured in accordance with a method according to claims 1 through 3.
9. Application of a solid according to claim 7 or 8 as sputter target.