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(54) Process for producing zinc sulfide

Verfahren zur Herstellung von Zinksulfid

Procédé de préparation de sulfure de zinc

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(73) Proprietor: **CVD INCORPORATED**
Woburn
Massachusetts 01801 (US)

(72) Inventors:
- **Goela, Jitendra Singh**
  Andover,
  Massachusetts 01810 (US)
- **Salihbegovic, Zlatko**
  New Iberia,
  Louisiana 70560 (US)

(74) Representative: **Kent, Venetia Katherine**
Rohm and Haas Europe Services ApS - UK Branch
European Patent Department
4th Floor, 22 Tudor Street
London EC4Y 0AY (GB)

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Description

BACKGROUND OF THE INVENTION

Field of the invention

[0001] Zinc sulfide is a durable material which intrinsically is transparent to relatively long electromagnetic wavelengths in the far-infrared range. These properties contribute to its use in applications which require infrared transmission capability such as in infrared detectors and missile domes. Zinc sulfide forms or articles are typically produced by chemical vapor deposition (CVD) or hot pressing techniques. These techniques result in forms which are generally opaque and not functionally transparent in the visible or near-infrared regions of the electromagnetic spectrum. Hot-isostatic pressing (HIP) has been found to sufficiently improve the transparency of zinc sulfide articles in the visible and near-ultraviolet regions that these forms can be used in applications requiring multi-spectral capability, such as in tank and aircraft windows. However, the visual transparency and clarity of such articles is less than desirable restricting the use of these articles in applications which require optical clarity. This invention relates to improvements in the CVD process which result in articles having significantly improved visual clarity after HIP treatment.

Description of related art

[0002] Chemical vapor deposition has been used to produce zinc sulfide in bulk form or in the form of a layered coating on a substrate. Typically such production involves the reaction of H_2S with vaporized zinc in proximity to either a substrate or a mandrel box on which the zinc sulfide deposits, such as is described in U.S. Patent No. 5,686,195. The zinc sulfide deposits produced by this CVD method generally exhibit poor transmission in the visible and near-infrared regions of the electromagnetic spectrum. The transmission properties in these regions can be substantially improved by hot isostatic pressing (HIP) of the CVD produced form as described in U.S. Patent No. 4,944,900.

[0003] A moderately clear ZnS has previously been commercially produced by a two-step process. First, elemental zinc vapors are reacted with hydrogen sulfide at a H_2S/Zn molar ratio of 1, a mandrel temperature of 735°C and an absolute pressure of 35 torr, in a CVD reactor. Zinc sulfide is deposited on the mandrel until a deposit of the desired thickness is produced. The deposit is separated from the mandrel to provide a zinc sulfide form which is then HIP treated for up to 100 hours at 900-1000°C and pressures of 103.4 to 206.8 MPa (15,000-30,000 psi). While the clarity of an image transmitted through the zinc sulfide form is substantially improved by the HIP treatment, it is not adequate for applications requiring image transmission through relatively thick forms or for optical applications with prisms or the like. Such clarity of image is related to the forward scatter value of a beam from a He-Ne laser as measured by a scatterometer. The forward scatter of zinc sulfide products of the above noted HIP treatment have typically varied between 10 and 40% cm^{-1}. For imaging applications, such as required in military aircraft and vehicles, the scatter value should be as low as possible, many such applications requiring scatter values less than 7% cm^{-1}. Previous attempts to improve these scatter values resulted in increased inclusions in the material, which degrade its transmission and optical quality, and also produced bowing, or induced curvature, in the material, which can cause cracking and reduce the yield of flat plates.

[0004] Accordingly, a need has existed for a reliable method of producing zinc sulfide articles having improved transmission and clarity in the visible and near-infrared electromagnetic wavebands, while avoiding increasing inclusions and/or bowing in the product articles. The present invention provides zinc sulfide articles having enhanced extended transparency in the visible range which permits their use in optical applications, such as for lenses, prisms, windows, etc., and other applications which take advantage of its high refractive index.

[0005] Moreover, bulk materials derived from CVD produced deposits often encounter induced curvature, or bowing, which, as with the zinc sulfide products discussed above, can result in cracks appearing in the product as well as reducing the yield of flat plates or articles. Accordingly, a general need exists for improved CVD processes which reduce the incidence and severity of bowing in the bulk product.

[0006] The present invention aims to achieve these objects by means of the process defined in claim 1.

[0007] The invention provides a method of producing high quality, water-clear, low scatter zinc sulfide (ZnS) articles having greatly improved scatter, transmission and visual/optical quality features. Modification of the processing conditions of the CVD process, while continuing the same conditions as used before in the HIP process, has resulted in water-clear zinc sulfide articles having high visible and near-infrared wavelength transmission, controlled bowing and forward scatter values consistently less than 7% cm^{-1}.

[0008] The modified CVD process conditions include (a) lowering the mandrel, or substrate, temperature from 735°C to lower operative processing temperatures, preferably less than 680°, with a higher initial temperature provided at the initiation of each run which is gradually ramped down to the intended processing temperature, (b) decreasing the H_2S/Zn molar ratio from 1 to a value less than 0.8, (c) initiating the flow of vaporized zinc to the deposition zone slowly at the beginning of each run by slowly ramping up the temperature of the vaporized zinc produced in the retort, and (d) maintaining the mandrel temperature at least 10°C above the temperature of the zinc in the retort.

BRIEF DESCRIPTION OF THE DRAWING

[0009] The drawing schematically illustrates a chemical vapor deposition furnace in which the present inventive process can be conducted.

DETAILED DESCRIPTION OF THE INVENTION

[0010] A furnace for producing sheets of CVD zinc sulfide is schematically illustrated in the Figure. The furnace 10 is enclosed in a vertically oriented water cooled stainless steel vacuum chamber housing 12. A graphite retort 14 containing molten zinc 15 and provided with a first heating means, such as resistance and/or radiant heating elements, is provided near the bottom of the chamber 12. A rectangular graphite mandrel 16 is arranged above the zinc retort 14 with its interior in flow communication with the retort. Second heating means 18 capable of heating the graphite mandrel are provided around the mandrel's exterior. A gas injector 20 provides hydrogen sulfide (H_2S) and an inert carrier gas to the lower portion of the mandrel's interior. The gas exhaust 22 at the top of the housing 12 is operatively connected to a filtration system (not shown) to remove particulates, then to a vacuum source, such as a vacuum pump (not shown) and finally to a scrubber (not shown) to remove unreacted H_2S and any other toxic products. The temperature of the mandrel is measured by a thermocouple 24 touching the mandrel at its external surface. The temperature of the zinc in the retort is measured by averaging the temperature measurements of two thermocouples, one 26 touching the upper portion of the retort's wall (above/near the level of molten zinc) and another thermocouple 28 extending to the lower portion of the retort's wall (below the level of molten zinc).

[0011] In operation, elemental zinc vaporized in the zinc retort 14 at a first temperature is mixed with the injected H_2S and carrier gas as they enter the mandrel 16. The mixed gases are caused to flow through the interior of the graphite mandrel wherein they contact the heated mandrel and are heated to a second, or substrate, temperature causing the zinc and H_2S to react forming ZnS on the interior surfaces of the mandrel 16. The carrier gas and any gaseous or entrained reaction products are removed from the chamber at the gas exhaust 22 and processed through the filtration and scrubbing systems. Once started, the process is continued until the desired thickness of zinc sulfide is deposited on the graphite mandrel, which takes more than 15 hours and can take up to 1100 hours, and typically takes between 100 and 600 hours. When the desired thickness is achieved the gas flow through the gas injector 20 is discontinued, the first heating means is turned down, the second heating means 18 is turned off, the chamber housing 12 is opened and the graphite mandrel 16 is removed. The zinc sulfide sheets deposited on the interior walls of the mandrel are then removed therefrom and cut into sheets of the desired size.

[0012] The sheets are machined to remove graphite contaminants on the substrate, or mandrel, side and are machined to smooth the deposition side. The sheets are then treated (hipped) by a HIP process which typically subjects them to high temperature (900° 1000°C) and isostatic high pressure 103.4 to 206.8 MPa (15,000-30,000 psi) for an extended time up to 150 hours.

[0013] The inventive improved process provides for initiating each run at a mandrel temperature (substrate temperature) of 690°C or higher, and gradually decreasing, or ramping down, the mandrel temperature by at least 10°C to a target mandrel temperature less than 680°C, and preferably within the range of 660°C to 680°C over the course of the first 5 to 20 hours of the run, preferably during the first 8 to 15 hours, and then maintaining the target mandrel temperature for the remainder of the run. We have found that by initially providing a higher mandrel temperature which is slowly ramped down to the target temperature, the nucleation density of the first deposited layer is decreased and bowing of the product sheet is diminished.

[0014] The present process also provides for sustaining a stoichiometric excess of zinc in the deposition zone after an initial ramping up of the zinc vapor concentration in the gas mixture supplied to the deposition zone. Previously, in a typical run, a H_2S/Zn molar ratio of 1 was provided to the deposition zone. While some previous runs had attempted H_2S/Zn molar ratios within the range of 0.6-0.75, the product of these runs had increased inclusion levels. The zinc vapor flow rate is dependent on the zinc retort temperature, the operating pressure, and the flow rate of the total feed gas mixture, including the H_2S and the carrier gas as well as the zinc vapor. Our process provides a H_2S/Zn molar ratio of less than 0.8, preferably of 0.6 to 0.8 after an initial ramping up of the zinc vapor concentration. During the initial ramping up the flow of zinc vapor is initiated at a minimal value at the beginning of each run and is slowly increased, or ramped up, to the target, or sustained, flow rate over the initial 10 to 90 hours and, preferably, over the initial 30 to 60 hours, of the run. Usually, such is accomplished by initially setting and then maintaining the H_2S and carrier gas flow rates while slowly ramping up the zinc retort temperature. We have found that this procedure minimizes up and down fluctuations in the zinc flow rate and minimizes minute deposits of zinc metal on the mandrel which, otherwise, would eventually appear as inclusions in the zinc sulfide article. This procedure provides a lower initial deposition rate and an initially decreasing H_2S/Zn molar ratio, both of which also contribute to controlling bowing in the product article.

[0015] Finally, in our process the zinc retort temperature is always maintained at least 10°C lower, preferably at least 15°C lower, and most preferably 20°C lower, than the mandrel, or substrate, temperature. This requirement has been found to diminish zinc condensation in the deposition zone, thereby further avoiding inclusions in the product.

[0016] The present process operates at a furnace absolute pressure of less than 60 torr, preferably 30 to 40 torr. The conditions of the previous post deposition HIP process are continued in the post treatment of the present CVD product.

Example 1

[0017] The zinc retort in a furnace similar to that illustrated in the Figure was initially heated to a temperature above 575°C. The absolute pressure in the furnace was adjusted to 35 torr. Argon was introduced as a carrier gas at a flow rate of 113.1 slpm (standard liters per minute). Hydrogen sulfide was provided at a flow rate of 9.3 slpm. The Zn vapor flow rate was ramped up to a target flow rate of 12.43 slpm by increasing the average zinc temperature in the retort from 597.5°C to 647°C during the first 72 hours of the run. These zinc and H_2S flow rates provide a H_2S/Zn molar ratio of 0.75, which ratio was maintained throughout the run. The initial furnace temperature of 687°C was ramped down to a target temperature of 672°C during the first 10 hours of deposition, whereby the furnace temperature was maintained at least 25°C, above the temperature of the zinc in the retort. The deposition was continued for 350 hours and resulted in 430kg (947 pounds) of deposited zinc sulfide. The average deposition rate was 53.6μm/h (0.00211 inch/hour).

[0018] The CVD product was cut into plates, which were machined to remove graphite contaminants from the substrate side and to smooth the deposition side. The plates were wrapped in platinum foil and then Hipped at 990°C and 144-8MPa (21,000 psi) for 70 hours. The plates were then lapped and polished. Inspection with a bright fiber optic light focussed from the side of the plate failed to reveal any inclusions >0.1 mm in diameter. Measurement of the forward scatter of ten 25.4mm (1 inch) diameter, 10.08 mm thick samples at a half cone angle of 0.5-3 degrees from the direction of a beam provided from a He-Ne laser (wavelength of 632.8nm or 0.6328 micron) in a scatterometer, provided scatter values in the range of 4.3 to 7.4 % cm^{-1}, with an average scatter value of 5.5% cm^{-1}. Transmission values measured with a spectrophotometer were 56.3 to 58.8% at the 450nm wavelength and 63.34 to 64.54% at the 550nm wavelength. Thus, the process provided a low scatter, high transmission zinc sulfide plate with no visible inclusions.

Example 2

[0019] In this example furnace pressure and Hipping conditions were the same as in Example 1. The average zinc temperature in the retort was ramped up during the first 50 hours of the deposition from 610.5°C to 651°C. The mandrel temperature was ramped down during the first ten hours of operation from 690°C to 674°C. The zinc target flow rate was 13.3 slpm, while the hydrogen sulfide and argon flow rates were the same as in Example 1, providing a H_2S/Zn molar ratio of 0.7. The deposition continued for 300 hours, during which the mandrel temperature exceeded the zinc retort temperature by at least 23°C.

[0020] Fifteen 0.8 cm thick samples demonstrated excellent inclusion quality with no inclusions >0.1 mm diameter detected. The forward scatter values ranged between 3.83-5.27% cm^{-1}, with an average value of 4.90% cm^{-1}. The visible transmission values ranged from 58.4% to 58.6% at the 450 nm wavelength, and from 64.7% to 66.1% at the 550 nm wavelength. Thus, lowering the H_2S/Zn molar ratio from 0.75 to 0.70 improved the average forward scatter values without affecting the optical quality.

Example 3

[0021] In this example the average zinc retort temperature was ramped up from 621.5°C to 648.5°C during the first sixteen hours of the deposition. The mandrel temperature was ramped down from 708°C to 676°C. The target flow rate of zinc vapor was 15.24 slpm, while the flow rates of hydrogen sulfide and argon were maintained as in Example 1, resulting in a H_2S/Zn molar ratio of 0.61. The furnace pressure was the same as in Example 1. The deposition continued for 350 hours during which a >25°C difference was maintained between the mandrel and zinc retort temperatures. The deposit was removed from the mandrel and Hipped at 990°C and 103.4 MPa (15,000 psi) for 90 hours.

Inspection of 0.83 thick samples rated them good for inclusion quality although they were not as good as the samples from Examples 1 and 2. Moreover, the product plates demonstrated greater bowing than the plates produced in Examples 1 and 2. Forward scatter values were in the range of 4.67 to 6.24 % cm^{-1}, with an average value of 4.85% cm^{-1}. The diminished bowing and inclusion quality is believed to be attributable to not providing sufficient time for ramping up the zinc vapor flow and to the relatively low value of the molar ratio.

Example 4

[0022] In this example the average zinc retort temperature was ramped up from 630.5°C to 648°C during the first 50 hours of the deposition. The mandrel temperature was ramped down from 689°C to 669°C over the first 10 hours of the deposition. The zinc vapor target flow rate was 14.1 slpm and the argon and H_2S flow rates were essentially the same as in the previous examples. This resulted in a H_2S/Zn molar ratio of 0.65. The furnace pressure and HIP conditions were essentially the same as in the preceding examples.

[0023] The plates produced from this run demonstrated less bowing than the plates produced from Example

3, but showed greater bowing than did the plates resulting from Example 2. The inclusion quality was excellent with no inclusions >0.1 mm detected.

[0024] The minimized bowing is believed to result from decreasing the nucleation density and from providing a gradual increase, or ramping up, of the ZnS deposition rate at the beginning of the deposition. The nucleation density is decreased by initially providing the mandrel at a temperature at least 10°C above its target temperature and gradually reducing its temperature to the target temperature over the first 10 or more hours of the deposition. A gradual increase of the deposition rate is usually accomplished by an initial gradual ramping up of the zinc flow rate controlled by initially gradually ramping up the zinc retort temperature over the initial 10 to 90 hours of the deposition.

[0025] Zinc sulfide plates produced by the inventive process which demonstrate forward scatter values of less than 7% cm.$^{-1}$ have been processed into optical prisms and thick windows and lenses having enhanced clarity and satisfactory performance otherwise. The plates produced prior to this invention were not considered to be suitable for processing into such articles because their optical clarity was insufficient for these applications.

Claims

1. A process for producing a clear zinc sulfide article, comprising:

(a) providing a substrate (16) in a chamber (12) maintained at a reduced pressure;
(b) providing a mixture of zinc vapor (Zn) and hydrogen sulfide (H_2S) in the vicinity of said substrate causing zinc sulfide to deposit on said substrate;
(c) providing an initial concentration of said zinc vapor to said mixture from a molten zinc source;
(d) providing said substrate at an initial temperature;
(e) gradually increasing the zinc vapor in said mixture from its initial concentration to its target concentration;
(f) gradually decreasing the temperature of said substrate to a target temperature;
(g) maintaining a H_2S/Zn molar ratio of up to 0.8 in said mixture after said zinc vapor in said mixture has reached its target concentration;
(h) maintaining at least 10°C separation between the temperature of said molten zinc and the temperature of said substrate;
(i) recovering said zinc sulfide deposit; and
(j) processing said recovered deposit to produce a clear zinc sulfide article.

2. A process according to claim 1 wherein:

the step of gradually increasing the zinc vapor in said mixture comprises gradually increasing the temperature of said molten zinc source to at least 10°C above its initial temperature.

3. A process according to claim 1 or claim 2 wherein:

the concentration of said zinc vapor in said mixture reaches its target concentration during the first 10 to 90 hours preferably the first 30 to 60 hours, following initiation of the deposition.

4. A process according to any preceding claim wherein:

said substrate reaches its target temperature during the first 5 to 20 hours preferably the first 8 to 15 hours, following initiation of the deposition.

5. A process according to any preceding claim wherein:

the initial temperature of said substrate is at least 690°C.

6. A process according to any preceding claim wherein:

said target temperature of said substrate is at least 10°C lower than said initial temperature of said substrate.

7. A process according to any preceding claim wherein:

said target temperature of said substrate is less than 680°C.

8. A process according to any preceding claim wherein:

said reduced pressure is less than 60 torr.

9. A process according to any preceding claim wherein:

said H_2S/Zn molar ratio is maintained at less than 0.8

10. A process according to claim 9 wherein:

said H_2S/Zn molar ratio is maintained within the range of 0.6 to 0.75.

11. A clear zinc sulfide article made by a process according to any preceding claim, is capable of transmitting a 0.6328 micron wavelength light beam from a He-Ne laser with less than 7.4% cm^{-1} forward scatter.

Patentansprüche

1. Verfahren zur Herstellung eines klaren Zinksulfidgegenstands, umfassend:

   (a) das Bereitstellen eines Substrats (16) in einer Kammer (12), gehalten bei einem verminderten Druck,
   (b) das Bereitstellen eines Gemisches von Zinkdampf (Zn) und Schwefelwasserstoff (H_2S) in der Nachbarschaft des Substrats, wodurch bewirkt wird, daß sich Zinksulfid auf dem Substrat abscheidet,
   (c) das Bereitstellen einer anfänglichen Konzentration des Zinkdampfs zu dem Gemisch von einer geschmolzenen Zinkquelle,
   (d) das Bereitstellen des Substrats bei einer anfänglichen Temperatur,
   (e) das graduelle Erhöhen des Zinkdampfes in dem Gemisch von dessen anfänglicher Konzentration zu dessen Zielkonzentration,
   (f) das graduelle Vermindern der Temperatur des Substrats auf eine Zieltemperatur,
   (g) das Beibehalten eines H_2S/Zn Molverhältnisses von bis zu 0,8 in dem Gemisch, nachdem der Zinkdampf in dem Gemisch dessen Zielkonzentration erreicht hat,
   (h) das Beibehalten von mindestens 10°C Abstand zwischen der Temperatur des geschmolzenen Zinks und der Temperatur des Substrats,
   (i) das Rückgewinnen der Zinksulfidabscheidung und
   (j) das Verarbeiten der zurückgewonnenen Abscheidung unter Erzeugung eines klaren Zinksulfidgegenstands.

2. Verfahren gemäß Anspruch 1, wobei:

   der Schritt des graduellen Erhöhens des Zinkdampfes in dem Gemisch das graduelle Erhöhen der Temperatur von der geschmolzenen Zinkquelle auf mindestens 10°C oberhalb von dessen anfänglicher Temperatur umfaßt.

3. Verfahren gemäß Anspruch 1 oder Anspruch 2, wobei:

   die Konzentration des Zinkdampfes in dem Gemisch dessen Zielkonzentration während der ersten 10 bis 90 Stunden, vorzugsweise der ersten 30 bis 60 Stunden, erreicht, gefolgt von der Initiierung der Abscheidung.

4. Verfahren gemäß einem vorhergehenden Anspruch, wobei:

   das Substrat dessen Zieltemperatur während der ersten 5 bis 20 Stunden, vorzugsweise der ersten 8 bis 15 Stunden, erreicht, gefolgt von der Initiierung der Abscheidung.

5. Verfahren gemäß einem vorhergehenden Anspruch, wobei:

   die anfängliche Temperatur des Substrats mindestens 690°C ist.

6. Verfahren gemäß einem vorhergehenden Anspruch, wobei:

   die Zieltemperatur des Substrats mindestens 10°C niedriger als die anfängliche Temperatur des Substrats ist.

7. Verfahren gemäß einem vorhergehenden Anspruch, wobei:

   die Zieltemperatur des Substrats weniger als 680°C beträgt.

8. Verfahren gemäß einem vorhergehenden Anspruch, wobei:

   der verminderte Druck weniger als 60 Torr beträgt.

9. Verfahren gemäß einem vorhergehenden Anspruch, wobei:

   das H_2S/Zn Molverhältnis bei weniger als 0,8 gehalten wird.

10. Verfahren gemäß Anspruch 9, wobei:

    das H_2S/Zn Molverhältnis innerhalb des Bereichs von 0,6 bis 0,75 gehalten wird.

11. Klarer Zinksulfidgegenstand, hergestellt durch ein Verfahren gemäß einem vorhergehenden Anspruch, welches befähigt ist, einen 0,6328 μm Wellenlängenlichtstrahl aus einem He-Ne Laser mit weniger als 7,4% cm^{-1} vorwärtiger Streuung zu transmittieren.

Revendications

1. Procédé pour la production d'un article transparent en sulfure de zinc comprenant :

   (a) la fourniture d'un substrat (16) dans une chambre (12) maintenue à une pression réduite ;
   (b) la fourniture d'un mélange de vapeur de zinc (Zn) et de sulfure d'hydrogène (H_2S) au voisinage dudit substrat occasionnant le fait que du

sulfure de zinc se dépose sur ledit substrat ;
(c) la fourniture d'une concentration initiale desdites vapeurs de zinc audit mélange à partir d'une source de zinc fondu ;
(d) la fourniture dudit substrat à une température initiale ;
(e) l'augmentation progressive des vapeurs de zinc dans ledit mélange à partir de sa concentration initiale jusqu'à sa concentration ciblée ;
(f) la diminution progressive de la température dudit substrat jusqu'à une température ciblée ;
(g) le maintien d'un rapport molaire H_2S/Zn jusqu'à 0,8 dans ledit mélange après que lesdites vapeurs de zinc dans ledit mélange ont atteint leur concentration ciblée ;
(h) le maintien d'une séparation d'au moins 10°C entre la température dudit zinc fondu et la température dudit substrat ;
(i) la récupération dudit dépôt de sulfure de zinc ; et
(j) le traitement dudit dépôt récupéré pour produire un article transparent en sulfure de zinc.

2. Procédé selon la revendication 1, dans lequel :

l'étape d'augmentation progressive des vapeurs de zinc dans ledit mélange comprend l'augmentation progressive de la température de ladite source de zinc fondu jusqu'au moins 10°C au-dessus de sa température initiale.

3. Procédé selon la revendication 1 ou la revendication 2, dans lequel :

la concentration desdites vapeurs de zinc dans ledit mélange atteint sa concentration ciblée pendant les premières 10 à 90 h, de préférence les premières 30 à 60 h, suivant l'initiation du dépôt.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel :

ledit substrat atteint sa température ciblée pendant les premières 5 à 20 h, de préférence les premières 8 à 15 h, suivant l'initiation du dépôt.

5. Procédé selon l'une quelconque des revendications précédente,s dans lequel :

la température initiale dudit substrat est d'au moins 690°C.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel :

ladite température ciblée dudit substrat est au moins 10°C inférieure à ladite température initiale dudit substrat.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel :

ladite température ciblée dudit substrat est inférieure à 680°C.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel :

ladite pression réduite est inférieure à 60 torr.

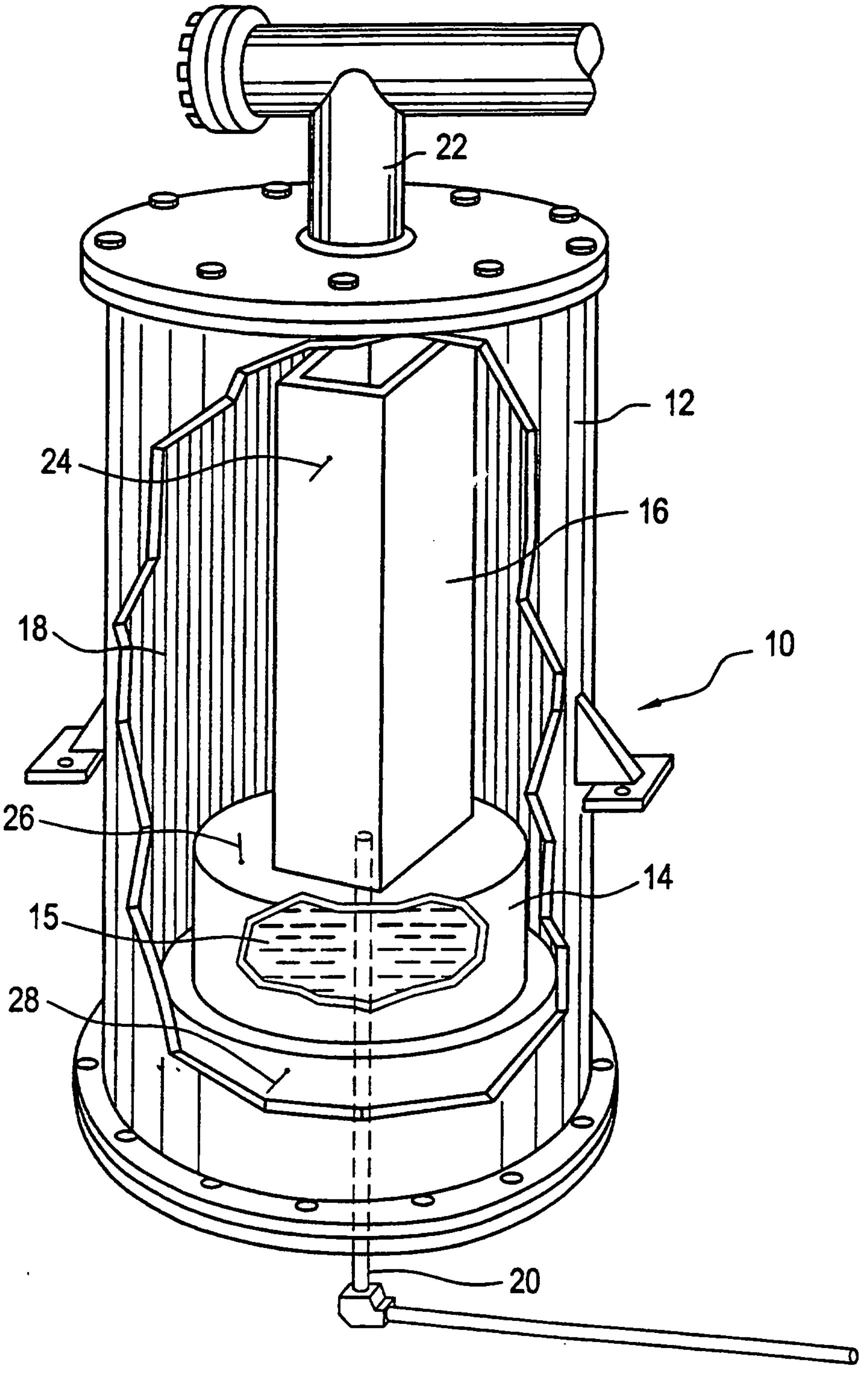
9. Procédé selon l'une quelconque des revendications précédentes, dans lequel :

ledit rapport molaire H_2S/Zn est maintenu à moins de 0,8.

10. Procédé selon la revendication 9, dans lequel :

ledit rapport molaire H_2S/Zn est maintenu dans l'intervalle de 0,6 à 0,75.

11. Article transparent en sulfure de zinc fabriqué par un procédé selon l'une quelconque des revendications précédentes, capable de transmettre un faisceau de lumière de longueur d'onde de 0,6328 micron à partir d'un laser He-Ne avec moins de 7,4 % cm^{-1} de diffusion vers l'avant.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