



(51) International Patent Classification:

C23C 14/08 (2006.01) B22F 3/10 (2006.01)  
C04B 35/453 (2006.01) C23C 4/11 (2016.01)

(21) International Application Number:

PCT/US2018/055935

(22) International Filing Date:

15 October 2018 (15.10.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/573,016 16 October 2017 (16.10.2017) US

(71) Applicant: MATERIALS SCIENCE INTERNATIONAL, INC. [US/US]; 1660 Georgesville Road, Columbus, Ohio 43228 (US).

(72) Inventors: SLAGEL, David; 1660 Georgesville Road, Columbus, Ohio 43228 (US). BRUCE JR., Thomas J.; 1660 Georgesville Road, Columbus, Ohio 43228 (US).

(74) Agent: KOCH, Ronald J. et al.; Eley Law Firm Co., LPA, 597 High St #388, Worthington, Ohio 43085-0388 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

(54) Title: ZINC STANNATE SPUTTER TARGET PRODUCTION METHODOLOGY

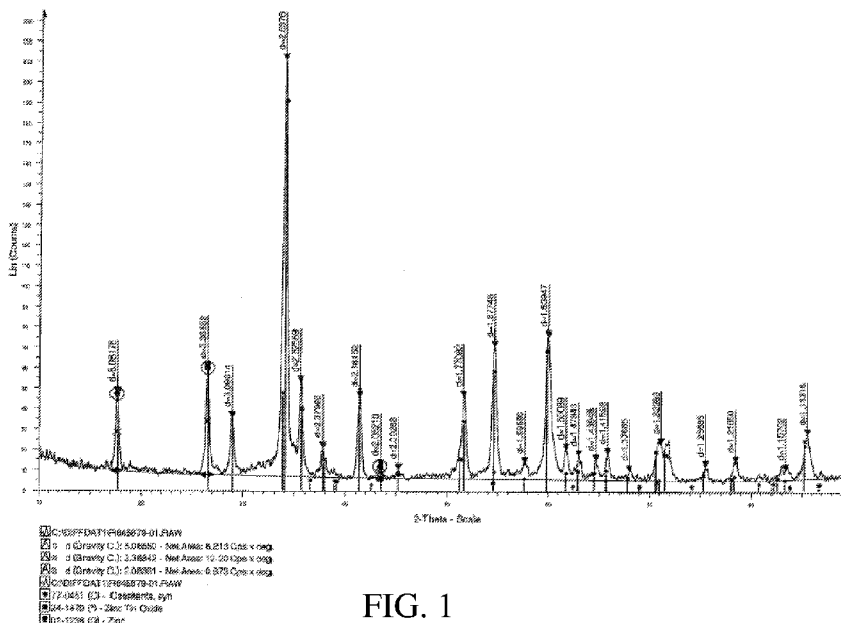


FIG. 1

(57) Abstract: A system and method for producing a sputter target by thermally spraying Zinc Stannate in the meta-stable form in a plasma stream to coat the sputter target. The subject technology employs various methods of pre-treatment of Zinc Stannate in the meta-stable form prior to thermal spraying, in order to favorably affect particle size, shape, and partial conversion of the meta-stable form to the stable form.



TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,  
KM, ML, MR, NE, SN, TD, TG).

**Published:**

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

## ZINC STANNATE SPUTTER TARGET PRODUCTION METHODOLOGY

### Cross-Reference to Related Applications

This application claims priority to U.S. provisional application 62/573,016, filed October  
5 16, 2017, the entire contents of the application being incorporated by reference.

### Field

The present invention relates generally to methods of production of sputter targets and specifically to such methods that incorporate Zinc Stannate.

### Background and Summary

10  $Zn_2SnO_4$  is a transparent conductive oxide. It is desirable to obtain a sputter target comprising pure  $Zn_2SnO_4$ . It should be understood that “purity”, or the like, as used herein, refers to the amount of  $Zn_2SnO_4$  present in the end product (aka sputter target), and that “impurity” or the like, refers to an end product having undesired constituents (e.g.  $ZnSnO_3$ ). Such purity is advantageous for various reasons. For example, there is a direct correlation between purity levels  
15 and conductivity affecting mitigation of negative factors such as arcing of the sputter target. Various factors have traditionally proven problematic in creating such a sputtering target comprising pure Zinc Stannate in the stable form. It has been discovered that thermally spraying  $ZnSnO_3$  as opposed to a mixture of  $ZnO + SnO_2$  (e.g.  $2ZnO + SnO_2$ ) as plasma yields surprising and unexpectedly improved purity levels on the sputter target.

20

### Description of Figures

Fig. 1 depicts an x-ray diffraction scan of a sample created using the subject technology.

Fig. 2 depicts a digital photomicrograph of a sample created using the subject technology.

Fig. 3 depicts a powder sample that was sintered at 2900 F.

Fig. 4 depicts a powder sample that was sintered at 2100 F.

Fig. 5 depicts a powder sample that was sintered at 1500 F.

Fig. 6A depicts an hypothetical equation using an inferior methodology.

Fig. 6B depicts an equation according to one aspect of the subject technology.

5 Fig. 6C depicts an equation according to another aspect of the subject technology.

Fig. 6D depicts an equation according to yet another aspect of the subject technology.

Fig. 7 depicts g/mole characteristics applicable to equations of Figs. 6A through 6D, & 8.

Fig. 8 depicts an equation according to yet another aspect of the subject technology.

Fig. 9A depicts a flow diagram according to one aspect of the subject technology.

10 Fig. 9B depicts a flow diagram according to another aspect of the subject technology.

Fig. 9C depicts a flow diagram according to yet another aspect of the subject technology.

Fig. 9D depicts a flow diagram according to yet another aspect of the subject technology.

Fig. 9E depicts a flow diagram according to yet another aspect of the subject technology.

### Description

15 Fig. 6A depicts an hypothetical equation using an inferior methodology wherein  $2\text{ZnO} + \text{SnO}_2$  are thermally sprayed to create  $\text{Zn}_2\text{SnO}_4$ . However, implementing this methodology has proven difficult in that relatively high doping and impurities are present in the end product, including residual  $\text{ZnSnO}_3$ .

20 Using the methodology of Fig. 6A, the spray undergoes an intermediate form of  $\text{ZnSnO}_3$  (the meta-stable form) during the plasma phase before being partially converted into the desired stable form of  $\text{Zn}_2\text{SnO}_4$ . Thus, the spray must undergo two conversions. It has been discovered that thermal spraying  $\text{ZnSnO}_3$  in the meta-stable form is superior to spraying  $2\text{ZnO} + \text{SnO}_2$ , at least because the intermediate form is avoided (there is only one conversion) during the plasma

phase, and because the improved method yields a relatively higher purity of the stable phase on the sputter target. Other advantages are achieved as well, including improved electrical conductivity and mechanical integrity.

Figs. 6B-D and Fig. 8 depict various aspects of the improved process of the subject technology which leads to a relatively more pure sputter target. As shown in Fig. 6C, a level of purity relatively higher than the equation of Fig. 6B is achieved by thermally spraying a combination of  $ZnO + 2ZnSnO_3$ . As shown in Fig. 6D, an level of purity relatively higher than the equation of Fig. 6C is achieved by thermally spraying a combination of  $2ZnO + 2ZnSnO_3$ .

Various techniques are employed using the subject technology relative to pre-processing of the substance to be thermally sprayed in order to facilitate the thermal spraying process and mitigate undesirable characteristics of the substance including missized and misshapen (e.g. non-spherically shaped) particles. Spray drying, agglomeration, and sintering are used in various aspects of the subject technology to affect such undesirable characteristics and to achieve a more flowable substance. In one aspect, ZnO is added to ZnSnO<sub>3</sub> before agglomerating and sintering.

Pre-processing (e.g. agglomerating and sintering) ZnSnO<sub>3</sub> at an optimum level for conversion to stable phase (aka cubic spinel phase) of Zn<sub>2</sub>SnO<sub>4</sub> can have a dramatic impact on plasma spray deposit rates, mechanical properties, and electrical conductivity of the final product. The percent of non-converted ZnSnO<sub>3</sub> remaining after pre-processing is optimized in one aspect to a range of between 20% and 90%, and in another aspect between 35% and 85%.

The particle size of the metastable ZnSnO<sub>3</sub> (the pre-thermally sprayed substance) affects conversion to the desired stable Zn<sub>2</sub>SnO<sub>4</sub>. The various pre-treatment techniques as described herein are useful for controlling the particle size and flowability of the substance to be thermally sprayed. In one aspect, a particle size of between 20 to 130 microns is used. In one aspect,

chemically synthesized  $\text{ZnSnO}_3$ , having a particle size of around 130 microns is sintered and then thermal sprayed. In some aspects, the final stoichiometry is tailored by adding ZnO to  $\text{ZnSnO}_3$ .

Theoretically, the  $\text{ZnSnO}_3$  meta-stable molecule transforms to the more stable cubic spinel phase ( $\text{Zn}_2\text{SnO}_4$ , aka “cubic spinel”) when heated to above 600 degrees Celsius. A typical plasma spray operation can result in temperatures up to 10,000 degrees C and above. Therefore,  $\text{ZnSnO}_3$  meta-stable phase that is sprayed through a plasma gun is subject to conversion to the stable phase of  $\text{Zn}_2\text{SnO}_4$ .

The temperature and temporal duration of sintering affects the optimization of morphology and particle size to facilitate thermal spraying. It is important to note that there is an optimum range of conversion from the meta-stable phase to the stable phase during sintering. In other words, there is a point past which too much of the substance has been converted and there is a point before which too little has been converted, and there is an intermediate range that yields a substance suitable for thermal spraying according to the subject technology. It has been discovered that sintering at 1500 deg F (approx 816 deg C, shown in Fig. 5) yielded poor results, including inefficient spraying; sintering at 2900 deg F (approx 1593 deg C, shown in Fig. 3) yielded poor results, including inefficient spraying, with an almost crystalized material not suitable for spraying; however, sintering at 2100 deg F (approx 1149 deg C, shown in Fig. 4) yielded favorable results, resulting in a partially converted material (around 20-80% converted) that was suitable for thermal spraying. In one aspect, sintering is performed at 2100 deg F for between 6-12 hours.

Fig. 3 depicts a powder sample that was sintered at 2900 deg F. This sample was heavily converted from the zinc stannate meta-stable to the zinc stannate stable. The powder did not spray efficiently.

Fig. 4 depicts a powder sample that was sintered at 2100 F. This material converted  
5 between 20% and 80% and it sprayed efficiently.

Fig. 5 depicts a powder sample that was sintered at 1500 F. This material had lower conversion to the stable phase and it did not spray efficiently.

Fig. 8 depicts a two-step process wherein  $ZnSnO_3$  is sintered before thermal spraying. During sintering, about one-half of the  $ZnSnO_3$  is converted to  $Zn_2SnO_4 + SnO_2$  with the other  
10 half remaining as  $ZnSnO_3$  until thermal spraying after which it is converted to  $ZnSnO_4 + SnO_4$ . Converting some of the  $ZnSnO_3$  to  $Zn_2SnO_4$  before thermal spraying has a positive effect on the overall purity of the end product.

Commercially available Zinc Stannate [e.g. (CAS No. 12036-37-2) Molecular Formula:  $O_3SnZn$ ] generally comprises particles sized at around 5 micron or less. The subject technology  
15 requires larger particle sizes. Thus, various techniques of pre-processing as described herein are employed to obtain a more suitable particle size. In one aspect, Zinc Stannate of 2 to 4 micron size is processed before thermal spraying to obtain a relatively more spherical and free flowing product. In one aspect, optimal measurable powder characteristics are as follows: D10-45  
micron, D50-78 micron, D90-120 micron, the particle size distribution being: 120 micron-10% ,  
20 75 micron -40%, 63 micron- 40%, 45 micron- 10%, and less than 35 micron-0%.

In one aspect,  $ZnSnO_3$  powder having a purity of 99.9% by weight is used as the starting material. In another aspect, this powder can be doped with other compounds of suitable powder size. In one aspect, the powder is free of all flow aids. In one aspect, doping material consists of

one constituent (e.g. metallic or ceramic with 99.9% purity), producing a blended powder comprising two discreet constituents. In one aspect, two discreet powders are blended to obtain a homogeneous blend of 99% ZnSnO<sub>3</sub> and 1% SnO<sub>2</sub>, considered to be a blended elemental as opposed to a composite particle. Such a powder adapted to flow in a plasma spray process is  
5 suitable for use in producing a Zn<sub>2</sub>SnO<sub>4</sub> sputter target.

In one aspect, plasma guns employed use a mixture of gases to optimize the final percentage of end product in the sputter target, with the option to include oxidizing gases, reducing gases, or inert gases to the gas mixture. In one aspect, ZnSnO<sub>3</sub> is fed into a Praxair SG-100 Plasma gun with a mixture of Argon-Hydrogen gas. There are various reasons for using  
10 different gas mixtures (e.g. reaction chemistries and enthalpies). The powder is injected into a very hot plasma and is melted and accelerated to speed and then sprayed onto a substrate. The substrate can be any material (that will withstand sufficient temperatures), and the substrate can be any geometry. In one aspect, an intermediate layer is added between the material being sprayed and the substrate to aid in adhesion.

15 Fig. 1, depicts an x-ray diffraction (XRD) scan (y axis depicts the intensity of the x ray and the x axis depicts the Braggs angle of 2 theta). Fig. 2, depicts a digital photomicrograph which shows: Zn<sub>2</sub>SnO<sub>4</sub>-69.7% by volume with 0% of ZnSnO<sub>3</sub> and 0% of ZnO in the end product; the uniform large area depicted in Fig. 2 represents Zn<sub>2</sub>SnO<sub>4</sub>, a third phase is not shown, also noteworthy in Fig. 2 is the absence of cracking which, when present, results in less  
20 favorable electrical conductivity characteristics.

Using the methodology presented herein mitigates the potential of having un-reacted regions or islands of elemental SnO<sub>2</sub> and ZnO. Large areas of non-electrically conductive



regions reduce the overall electrical conductivity of the sputter target. This loss of conductivity will negatively impact the sputter performance of the target in service.

The teachings of the subject technology presented herein are beneficial for several reasons so stated herein and in the following table, and additionally such other benefits that will  
 5 apparent to those of skill in the art after having studied the subject technology.

Subject technology - benefits of starting with ZnSnO3 powder as opposed to a mixture	Disadvantages of conventional systems and methods using a mixture of ZnO and SnO
Produces a more homogenous/uniform morphology leading to superior electrical conductivity (lower resistance), and improved mechanical properties	Less homogenous morphology negatively impacts conductivity (higher resistance)
No mixing required between ZnO and SnO, therefore eliminating possibility of segregation or incomplete reaction	Mixing of SnO and ZnO leaves room for variation that can lead to incomplete conversion to Zn2SnO4
One step reaction in thermal spray process  Reaction 1: $2ZnSnO_3 \rightarrow Zn_2SnO_4 + SnO_2$	Two step reaction in thermal spray process  Reaction 1: $ZnO + SnO_2 \rightarrow ZnSnO_3$  Reaction 2: $2ZnSnO_3 \rightarrow Zn_2SnO_4 + SnO_2$
Electrical resistance of final product (as measured with 4 point probe) is relatively lower	Electrical resistance of final product (as measured with 4 point probe) is relatively higher

From the above description of the invention, those skilled in the art will perceive improvements, changes, and modifications in the invention. Such improvements, changes, and modifications within the skill of the art are intended to be covered.

-8-

What is claimed is:

1. A method of preparing a substance for thermal spraying a sputter target comprising the step of:
  - 5 providing ZnSnO<sub>3</sub> for the purpose of thermal spraying in order to create a plasma for coating the sputter target.
  
2. A method of preparing a substance for thermal spraying a sputter target comprising the step of:
  - 10 obtaining ZnSnO<sub>3</sub> for the purpose of thermal spraying in order to create a plasma for coating the sputter target.
  
3. A method of preparing a substance for thermal spraying a sputter target comprising the step of:
  - sintering ZnSnO<sub>3</sub> for the purpose of thermal spraying in order to create a plasma for coating the sputter target.
  
- 15 4. The method of claim 3 wherein:
  - the substance is sintered at a temperature of at least 600 deg C.
  
5. The method of claim 3 wherein:
  - the substance is sintered at a temperature of at least 600 deg C for at least three hours.

6. The method of claim 3 wherein:

the substance is spray-dried, then agglomerated, before sintering.

7. A substance for thermal spraying comprising:

ZnSnO<sub>3</sub> particles having a size of at least 20 microns.

5 8. The substance of claim 7 further comprising:

spherically shaped ZnSnO<sub>3</sub> particles.

9. A method of coating a sputter target comprising the step of:

thermally spraying ZnSnO<sub>3</sub> so as to create a plasma for coating the sputter target.

10. The method of claim 9 further comprising the step of:

10 thermally spraying a combination of ZnSnO<sub>3</sub> and ZnO.

11. A method of coating a sputter target comprising the step of:

thermally spraying a substance so as to create a plasma for coating the sputter target.

12. The method of claim 11 wherein:

15 the substance having been spray dried before thermal spraying.

13. The method of claim 12 wherein:

the substance comprises ZnSnO<sub>3</sub>.

-10-

14. The method of claim 11 wherein:

the substance having been agglomerated before thermal spraying.

15. The method of claim 14 wherein:

the substance comprises  $\text{ZnSnO}_3$ .

5 16. The method of claim 11 wherein:

the substance having been sintered before thermal spraying.

17. The method of claim 16 wherein:

the substance having been sintered at a temperature of at least 600 deg C.

18. The method of claim 16 wherein:

10 the substance having been sintered at a temperature of at least 600 deg C for at least three hours.

19. The method of claim 16 wherein:

the substance comprises  $\text{ZnSnO}_3$ .

20. The method of claim 11 wherein:

15 the substance having been spray-dried, then agglomerated, then sintered before thermal spraying.

-11-

21. The method of claim 20 wherein:

the substance comprises ZnSnO<sub>3</sub>.

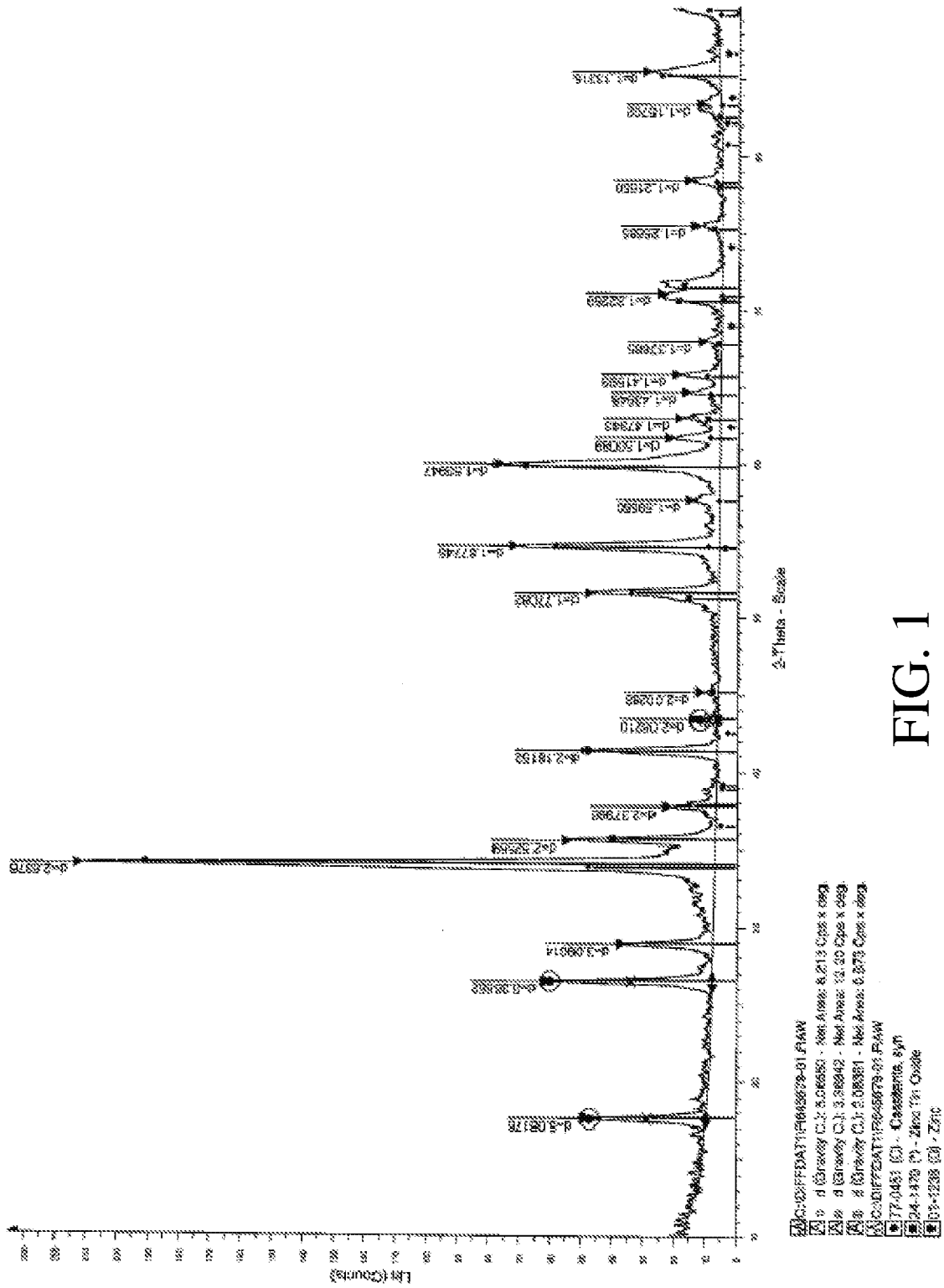


FIG. 1

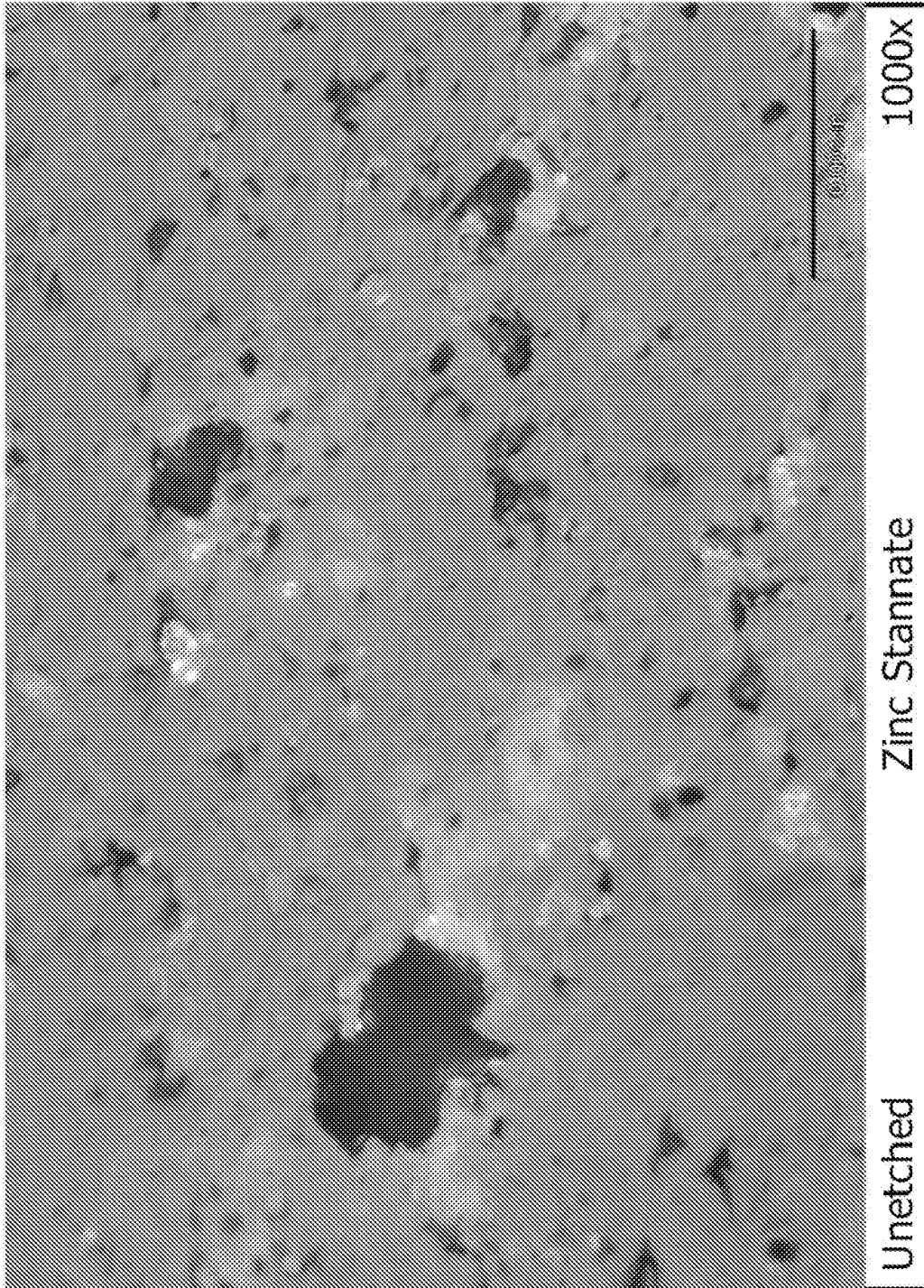


FIG. 2

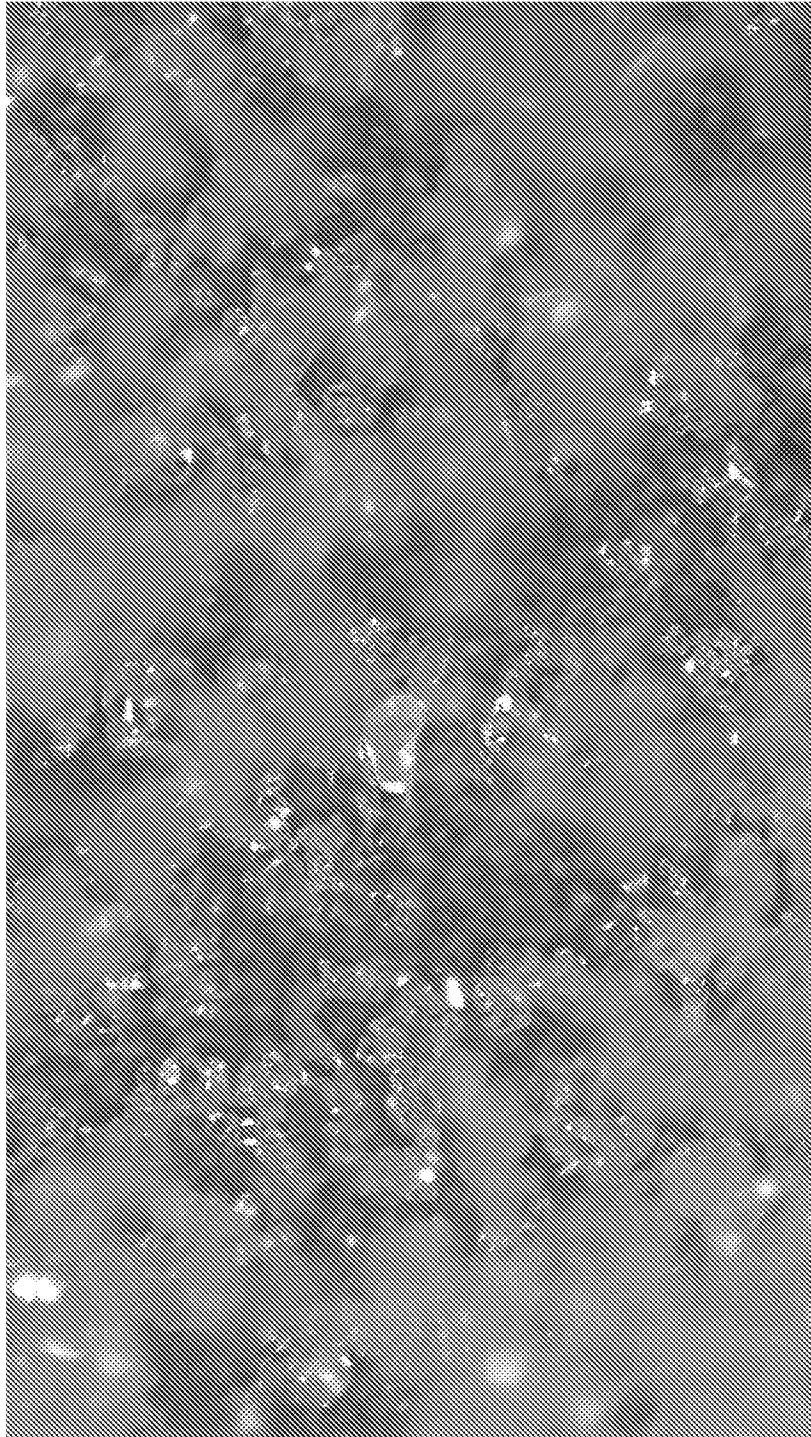


FIG. 3



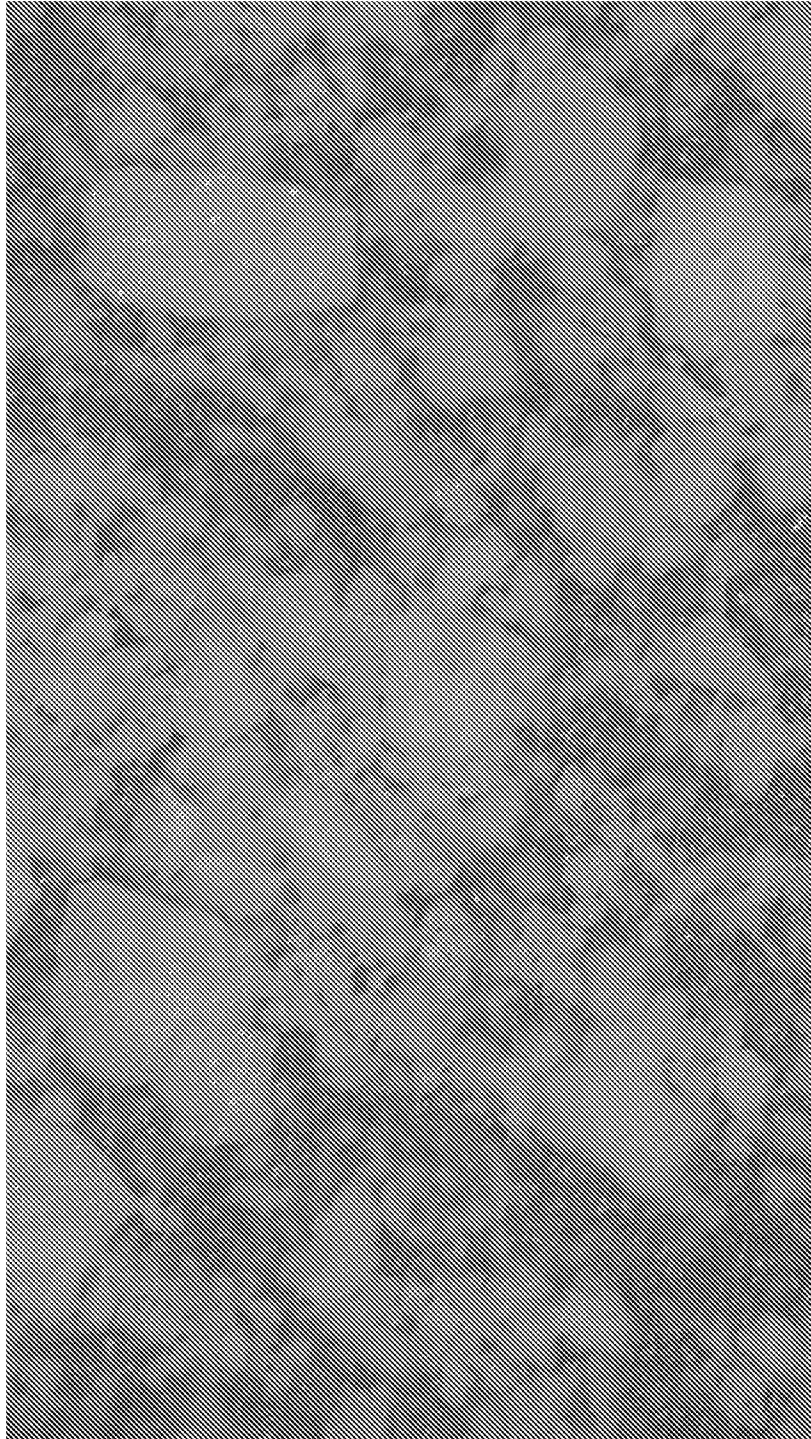


FIG. 4

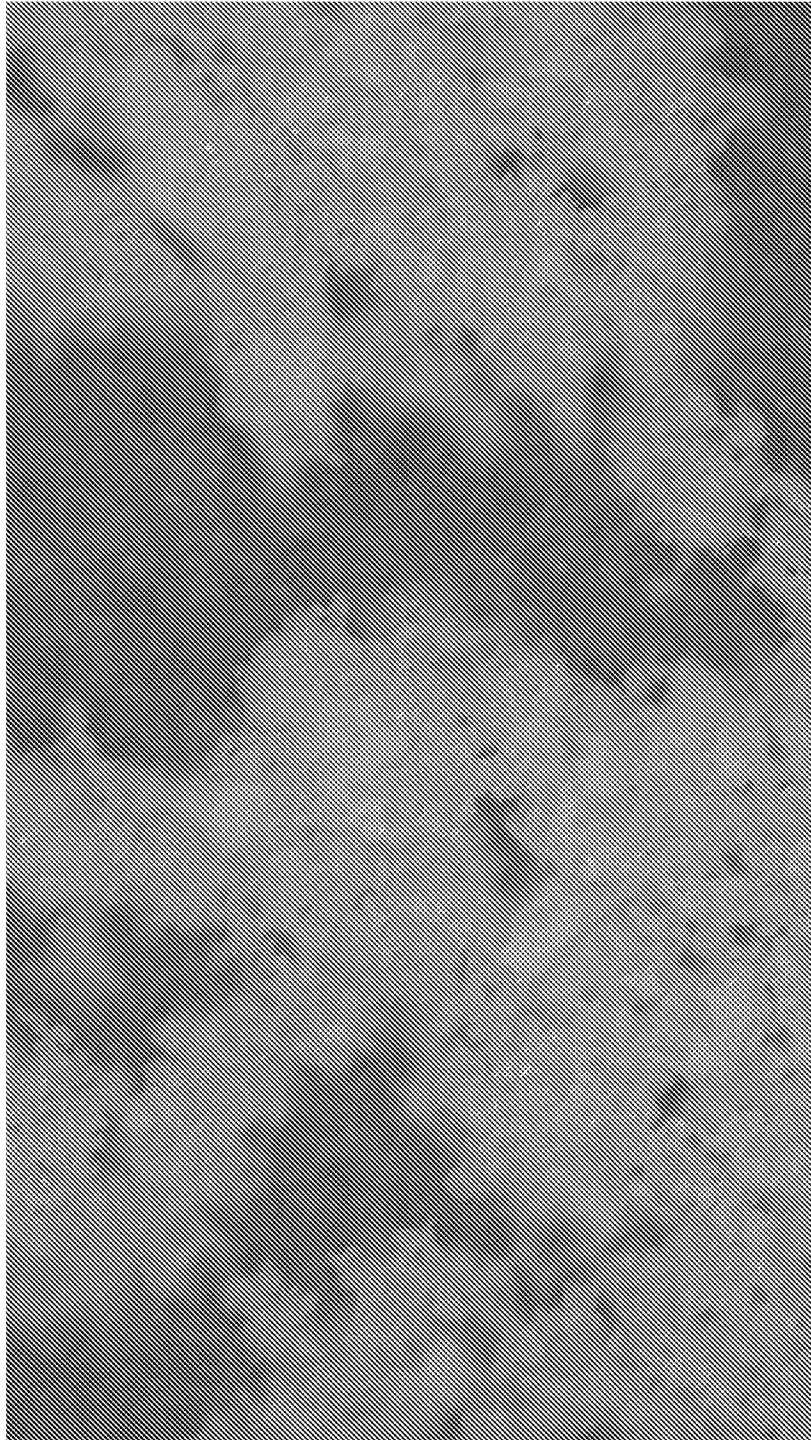
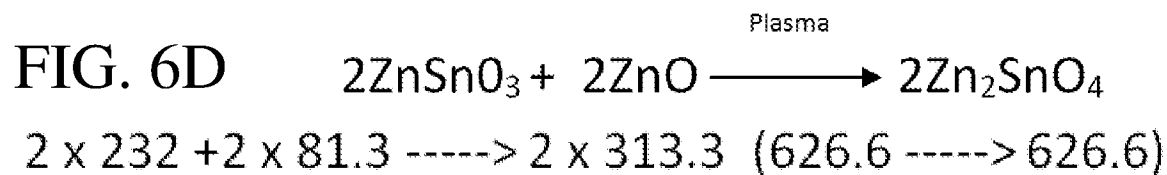
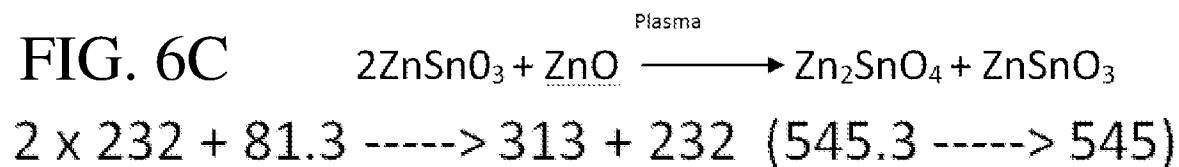
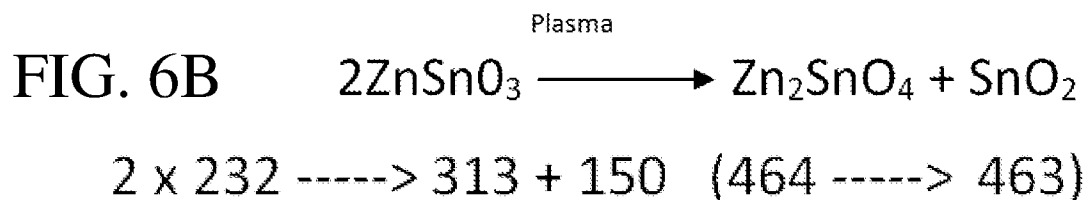
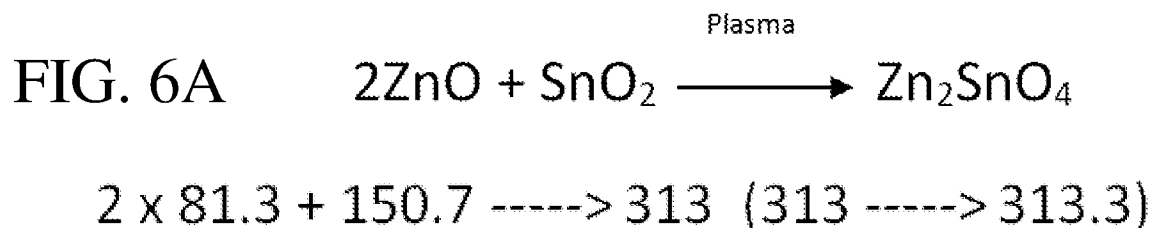


FIG. 5

6/9



7/9

Zn-	65.39	g/mole
Sn-	118.71	g/mole
O-	16	g/mole
ZnSnO <sub>3</sub> -	232	g/mole
Zn <sub>2</sub> SnO <sub>4</sub> -	313.3	g/mole
ZnO-	81.39	g/mole
SnO <sub>2</sub> -	150.7	g/mole

FIG. 7

8/9

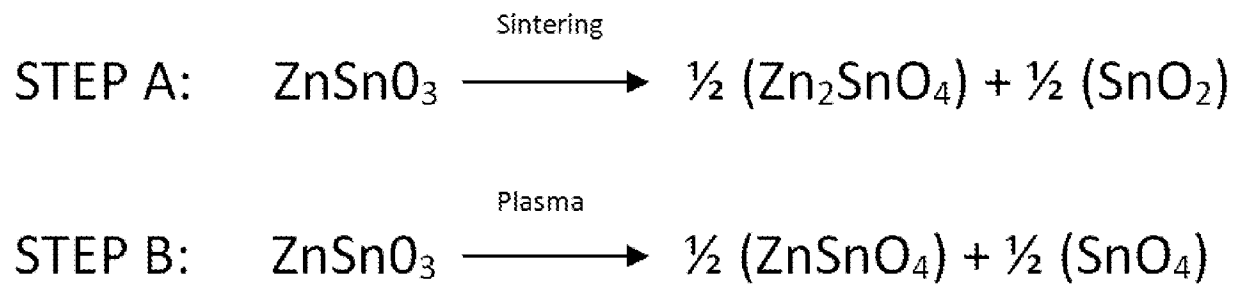


FIG. 8

FIG. 9A

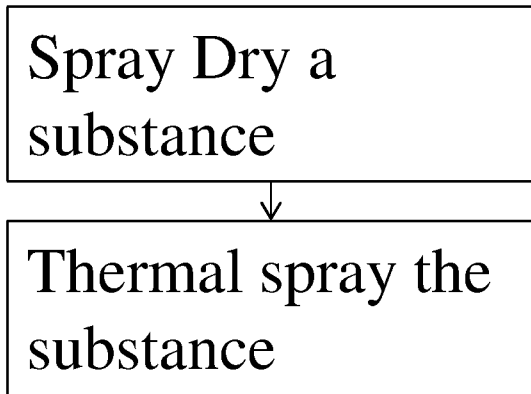


FIG. 9B

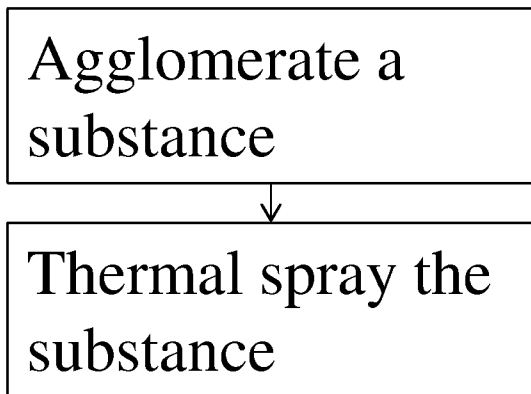


FIG. 9C

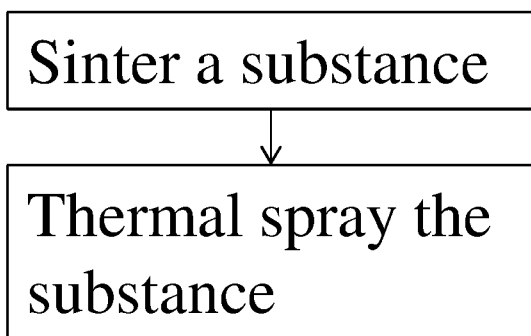


FIG. 9D

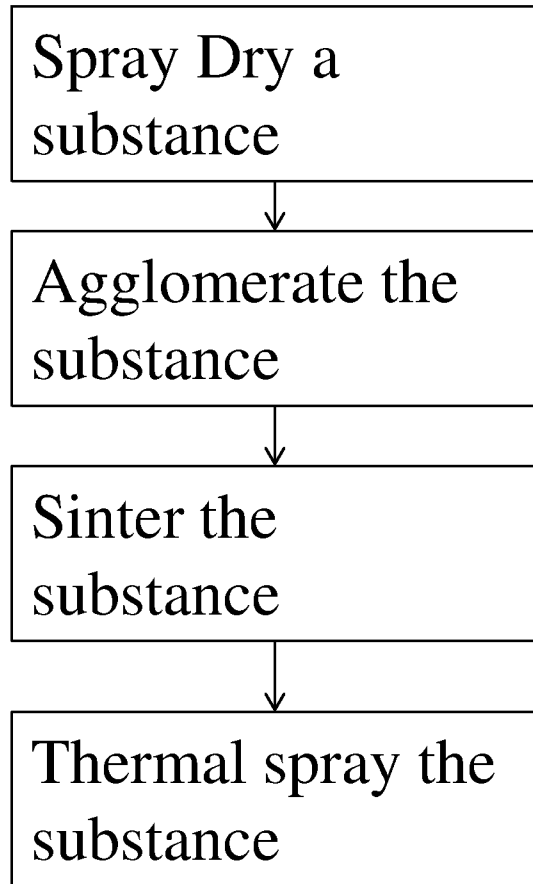
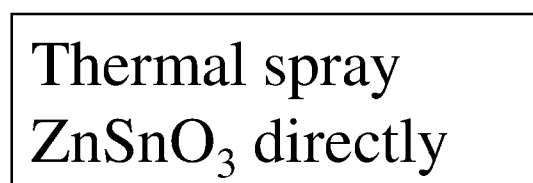


FIG. 9E



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2018/055935

A. CLASSIFICATION OF SUBJECT MATTER		
<b>C23C 14/08 (2006.01)</b> <b>C04B 35/453 (2006.01)</b> <b>B22F 3/10 (2006.01)</b> <b>C23C 4/11 (2006.01)</b>		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C23C 14/00, 14/06, 14/08, 14/22, 4/00, 4/11, C04B 35/00, 35/01, 35/453, 35/457, B22F 3/00, 3/10, 3/12		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PatSearch (RUPTO internal), USPTO, PAJ, Esp@cenet, DWPI, EAPATIS, PATENTSCOPE		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	EP 2953915 B1 (SOLERAS ADVANCED COATINGS BVBA) 16.11.2016, claims, example 6	1-5, 9-11, 13-19, 21 6, 8, 12, 20
X	US 2013/0234081 A1 (KOBELCO RESEARCH INSTITUTE, INC) 12.09.2013, claims	1-5, 9-11, 13-19, 21
Y	RU 94039287 A1 (X.K.SHTARPK GMBX UND KO, KG) 10.09.1996, abstract, claims	6, 12, 20
Y	SU 949918 A (NAUCHNO-ISSLEDOVATELSKIY INSTITUT POROSHKOVOJ METALLURGII BELORUSSKOGO POLITERHNICHESKOGO INSTITUTA) 30.04.1987, col. 2 lines 20-30	8
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents:		
“A”	document defining the general state of the art which is not considered to be of particular relevance	“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“E”	earlier document but published on or after the international filing date	“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“L”	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“O”	document referring to an oral disclosure, use, exhibition or other means	“&” document member of the same patent family
“P”	document published prior to the international filing date but later than the priority date claimed	
Date of the actual completion of the international search 04 February 2019 (04.02.2019)		Date of mailing of the international search report 14 February 2019 (14.02.2019)
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37		Authorized officer  N. Salenko  Telephone No. 8 499 240 25 91