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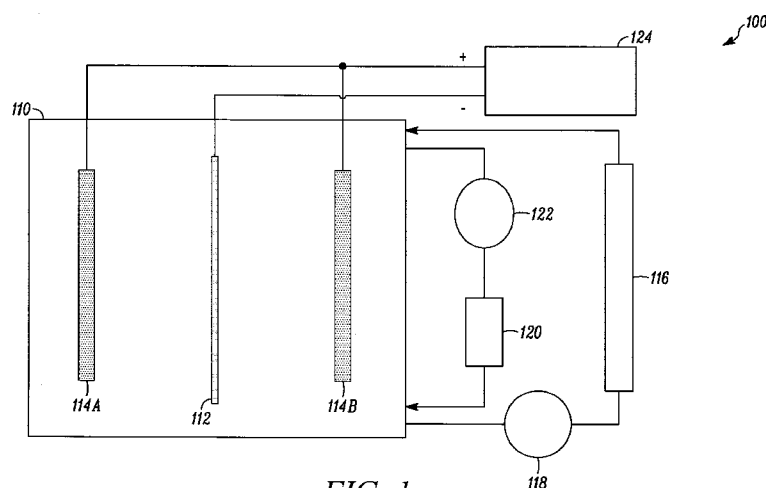
(54) **Title: REFINING PROCESS FOR PRODUCING LOW ALPHA TIN**

FIG. 1

(57) **Abstract:** A method for purifying tin includes exposing an electrolytic solution comprising tin to an ion exchange resin and depositing electrorefined tin from the electrolytic solution. The deposited electrorefined tin has alpha particle emissions of less than about 0.01 counts/hour/cm² immediately after the deposition step, and an alpha emissivity of less than about 0.01 counts/hour/cm² at least 90 days after the deposition step.



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REFINING PROCESS FOR PRODUCING LOW ALPHA TIN

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Non-provisional Application No. 13/800,506, filed March 13, 2013, U.S. Provisional Application No. 61/714,059, filed October 15, 2012, U.S. Provisional Application No. 61/670,960, filed July 12, 2012, and U.S. Provisional Application No. 61/661,863, filed June 20, 2012, each of which are herein incorporated by reference in their entirety.

FIELD OF THE INVENTION

[0001] The present invention relates to high purity tin with reduced alpha particle emissions for the manufacture of semiconductor equipment or the like and manufacturing methods for producing such high purity tin.

DESCRIPTION OF RELATED ART

[0002] Solders are commonly utilized in semiconductor device packaging and many other electronic applications. While conventional solders have been manufactured primarily from lead, more recent lead-free solders utilize tin and other metals as principal components.

[0003] One challenge with respect to the use of tin solders in electronic packaging applications is that the elemental tin materials used to manufacture solders contain varying levels of alpha particle emitting isotopes (also referred to as alpha particle emitters). Alpha particle emissions (also referred to as alpha flux) can cause damage to packaged electronic devices, and more particularly, can cause soft error upsets and even device failure in certain cases. This concern is compounded as device sizes are reduced and alpha emitting solder materials are closer to sensitive locations.

[0004] Uranium and thorium are well known as principal radioactive elements often present in metallic containing solders, such as tin solders, which may radioactively decay according to known decay chains to form alpha particle emitting isotopes. Of particular concern in tin materials is the presence of polonium-210 (^{210}Po), which is considered to be the primary alpha particle emitter responsible for soft error upsets. Lead-210 (^{210}Pb) is a decay daughter of uranium-238 (^{238}U), has a

half-life of 22.3 years, and β -decays to bismuth-210 (^{210}Bi). However, due to the very short 5.01 day half-life of ^{210}Bi , such isotope is essentially a transient intermediary which rapidly decays to ^{210}Po . The ^{210}Po has a 138.4 day half-life and decays to the stable lead-206 (^{206}Pb) by emission of a 5.304 MeV alpha particle. It is the latter step of the ^{210}Pb decay chain, namely, the decay of ^{210}Po to ^{206}Pb with release of an alpha particle that is of most concern in metallic materials used in electronic device applications.

[0005] Although ^{210}Po and/or ^{210}Pb may be at least in part removed by melting and/or refining techniques, such isotopes may remain as impurities in a tin material even after melting or refining. Removal of ^{210}Po from a tin material results in a temporary decrease in alpha particle emissions from the material. However, it has been observed that alpha particle emissions, though initially lowered, will typically increase over time to potentially unacceptable levels as the secular equilibrium of the ^{210}Pb decay profile is gradually restored based on any ^{210}Pb remaining in the metallic material.

[0006] Problematically, whether an increase in alpha particle emissions of a metallic material following a melting or refining process will eventually reach unacceptable levels is very difficult to assess and/or predict.

SUMMARY OF THE INVENTION

[0007] A method for purifying tin includes exposing an electrolytic solution comprising tin to an ion exchange resin and depositing electrorefined tin from the electrolytic solution. The electrorefined tin can have alpha particle emissions of less than about 0.01 counts/hour/cm² or less than about 0.002 counts/hour/cm². The ion exchange resin may include sulfonated, phosphomethylated, amino methyl phosphonic acid, and poly(4-vinyl-pyridine) functional groups and combinations of these functional groups. The electrolytic solution may have a pH of less than about 6 or about 1 or less.

[0008] The method for purifying tin may further include assessing the alpha particle emission potential of the electrorefined tin, including detecting alpha particle emissions from a sample of the deposited electrorefined tin, determining a concentration of a target parent isotope in the sample from the alpha particle

emissions detected in the detecting step and a time which has elapsed between the detecting step and the exposing and detecting steps, and determining a possible alpha emission of a target decay isotope of the target parent isotope from the determined concentration of the target parent isotope and the half-life of the target parent isotope.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Figure 1 is a block diagram of an electrorefining system.

[0010] Figure 2 is a plot of alpha particle emissions over time for electrorefined tin samples.

DETAILED DESCRIPTION

I. Method of Electrorefining Tin.

[0011] As described herein, tin may be electrorefined to produce refined tin having reduced alpha particle emissions or alpha flux when measured after the electrorefining process. The alpha particle emissions do not necessarily remain stable after the material has been subjected to an electrorefining process, and the alpha particle emissions may increase or decrease over time. As described herein, the refined tin may also have reduced alpha particle emissions when measured a period of time following the electrorefining process, such as 90 days after the electrorefining process. A method for determining the alpha particle emission potential, such as the maximum alpha particle emissions, for a refined tin is also described herein.

[0012] Tin may be electrorefined by depositing tin ions from an electrolytic solution onto a cathode by applying a current to the system. An electrolytic solution containing tin or stannous ions may be formed by dissolving or leaching tin in an acid electrolyte. For example, tin sulfate can be formed by an electrolytic dissolution of a 99.99% purity tin anode in an electrolyte including 1% to 10% sulfuric acid by volume mixed with deionized water. Suitable concentrations of soluble stannous ion in the electrolytic solution include but are not limited to from about 10 g/L to about 200 g/L. More particularly, suitable concentrations of soluble stannous ion in the electrolytic solution may be as low as 10, 20, 30, 40, 50, 60 g/L or as great as 80, 100, 120, 140, 160, 180 or 200 g/L or may be within any range delimited by any pair of the foregoing

values. At low tin concentrations, such as 40, 30, 20 g/L or less, the alpha particle emissions of the deposited material may be more sensitive to the current density of the electrorefining process than at higher tin concentrations

[0013] In certain embodiments, the electrolytic solution may be formed by adding a commercially available tin, such as commercially available tin having a purity level of 99.0% to 99.999% (2N to 5N), to the acidic electrolyte. In one example, the tin may have initial, pre-refining alpha particle emissions above about 0.001 counts/hour/cm². In other examples, the tin may have initial, pre-refining alpha particle emissions above about 0.002 counts/hour/cm², above about 0.005 counts/hour/cm², or above about 0.01 counts/hour/cm².

[0014] The electrolytic solution may include one or more acids. Suitable acids for use in the acidic electrolytic solution include but are not limited to hydrochloric acid, sulfuric acid, fluoroboric acid, acetic acid, methane sulfonic acid, and sulfamic acid. The acid may be mixed with water, such as diionized water. The acid(s) of the electrolytic solution can be selected to control the pH of the electrolytic solution.

[0015] The electrolytic solution may have a low, or acidic, pH. For example, an electrolytic solution having an acidic pH may have a pH of less than 7. In another example the electrolytic solution may have a pH of less than about 6. In a further example, the electrolytic solution may have a pH of less than about 5. In a still further example, the electrolytic solution may have a pH of less than about 4, less than about 3, less than about 2 or less than about 1. The pH of the electrolytic solution may be adjusted to optimize the effectiveness of the ion exchange resin and the electrorefining process.

[0016] The electrolytic solution may optionally include one or more additives. As used herein, an "additive" refers to a component of the electrolytic solution other than the target metal to be refined (e.g., tin), other metallic impurity components, and the acid/water solution. The additive may be helpful for controlling one or more properties of the electrolytic solution, the deposition process and/or the deposited product. Each additive may be present in amount from several parts-per-million (ppm) to several percent by weight. For example, each additive may be present in an amount of at least about 0.05% by volume of the electrolytic solution, at least

about 0.5% by volume of the electrolytic solution, or at least about 1.0% by volume of the electrolytic solution.

[0017] Suitable additives include antioxidants and grain refiners. For example, an antioxidant may be added to the electrolytic solution to prevent spontaneous Sn^{2+} to Sn^{4+} oxidation during electrolysis. Suitable antioxidants include, but are not limited to, phenol sulfonic acid and hydroquinone. Suitable commercially available antioxidants include Technistan Antioxidant, Techni Antioxidant Number 8 available from Technic, and Solderon BP Antioxidant available from Dow Chemical. Suitable concentrations of an antioxidant include from about 0.05% to about 10%, from about 0.5% to about 5%, or from about 1% to about 3% by volume of the electrolytic solution.

[0018] An organic grain refiner may optionally be added to the electrolytic solution to limit dendritic deposition at the cathode. Suitable organic grain refiners include, but are not limited to, polyethylene glycol. Suitable commercially available organic grain refiners include Technistan TP-5000 Additive, Techni Matte 89-TI available from Technic, and Solderon BP Primary available from Dow Chemical. Suitable concentrations of a grain refiner include from about 0.5% to about 20%, from about 1.0% to about 15%, or from about 3% to about 10% by volume of the electrolytic solution.

[0019] The electrolytic solution is exposed to at least one ion exchange resin during at least a portion of the electrorefining process. Ion exchange resins are organic compounds which include functional groups configured to selectively capture another material by exchanging ions with the captured material. For example, ion exchange resins may include functional groups bonded to a polymer matrix. In the current process, it is believed that the ion exchange resin captures and removes alpha emitting impurities from the electrolytic solution, such as metallic impurities and, in particular, metallic impurities which are either themselves capable of decay with concurrent release of an alpha particle, such as ^{210}Po , or metallic impurities which produce decay products with the decay products capable to decay with concurrent release of an alpha particle, such as U and/or Th.

[0020] In one example, the ion exchange resin may be placed in a column and the electrolytic solution may be circulated through the column. For example, the

electrolytic solution may be circulated from a tank, through the ion exchange resin column and returned to the tank by a pump. In this embodiment, the electrolytic solution may be circulated through the column of ion exchange resin concurrently with application of current to the electrolytic bath, or alternatively, the circulation of the electrolytic solution through the ion exchange resin may occur prior to, or after, application of current according to a desired quantify and/or duration. In a still further embodiment, circulation of the electrolytic solution through the ion exchange resin and application of current may be alternated as desired. The flow rate through the column may be adjusted to achieve a desired contact time between the electrolytic solution and the ion exchange resin. In an alternative embodiment, the resin may be added directly to the tank holding the electrolytic solution; a separate column is not used.

[0021] Suitable ion exchange resins may include at least functionalized carboxylic acid from the phosphonic acids group, such as amino methyl phosphonic acid functional groups. Further suitable ion exchange resins may include at least one functional group selected from sulfonated, phosphomethylated, amino methyl phosphonic acid, and poly(4-vinyl-pyridine) functional groups and mixtures thereof. Still further suitable ion exchange resins may include at least one functional group selected from sulfonated, phosphomethylated, amino methyl phosphonic acid, poly(4-vinyl-pyridine), sulfonic acid, chloromethyl, tributylamine, di-vinyl benzene, quaternary amine, divinylbenzene, diphosphonic acid, and iminodiacetate functional groups. Examples of commercially available suitable ion exchange resins are presented in Table 1, where “DVB” is divinylbenzene, “SB” is strong base, “SA” is strong acid, “WA” is weak acid, and “Dow” is Dow Chemical Company.

Table 1
Data for Select Ion Exchange Resins

Trade name	Vendor	Functional Group(s)	Exchange mechanism	Matrix
Monophos Resin	Eichrom	Sulfonated and phosphomethylated	Chelating	Styrene-DVB
Lewatit MonoPlus TP 260	Lanxess	Amino methyl phosphonic acid	Cation exchange	Crosslinked polystyrene
Reillex HPQ Polymer	Vertellus	Poly(4-vinyl-pyridine)	Anion exchange	DVB
Dowex G-26	Dow	Sulfonic acid	Cation exchange	Styrene-DVB, gel
Dowex Optipore L493	Dow	Chloromethyl	Adsorbent	Styrene-DVB, Macroporous
Dowex PSR-2	Dow	Quaternary amine	Anion exchange	Styrene-DVB, gel
Dowex 21K XLT	Dow	Quaternary amine	SB anion exchange	Styrene-DVB, gel
Dowex MAC-3	Dow	Carboxylic acid	WA cation exchange	Polyacrylic, macroporous
XZ 91419.00 resin	Dow	Quaternary amine	SB anion exchange	Styrene-DVB, gel
XUS 43568 resin	Dow	Di-methyl amine	WB anion exchange	Macro Styrene
Amberlyst A-26	Dow	Quaternary amine	Anion exchange	Styrene-DVB
Amberlyst 15WET	Dow	Sulfonic acid	SA cation exchange	Styrene-DVB, macroporous
Amberlite IRC-747	Rohm and Haas	Amino-phosphate; Na ⁺ form	Chelating	Styrene-DVB, macroporous
Amberlite PWA 5	Rohm and Haas	SB anion, NO ₃ ⁻ selective	Anion exchange	Cross-linked copolymer

Diphonix resin	Eichrom	Diphosphonic acid and sulfonic acid	Chelating	Styrene-based polymer
Lewatit TP 207	Lanxess	Iminodiacetate	Cation exchange	Crosslinked polystyrene

An ion exchange resin may be used alone or in combination with other ion exchange resins. In particular, a mixed bed resin may be used, where a mixed bed resin refers to a resin composition that includes two or more specific resins that may have the same or different functional groups, exchange mechanisms and/or matrices.

[0022] Tin from the electrolytic solution is plated onto a cathode during the electrorefining process. In some embodiments, exposing the electrolytic solution to the ion exchange resin and electrodeposition of the tin onto the cathode may occur at least partially concurrently. As described further below, the electrorefined tin may have reduced alpha particle emissions or alpha flux.

[0023] Figure 1 is a block diagram illustrating an exemplary continuous tin electrorefining system 100 including tank 110, cathode 112, first tin anode 114A and second tin anode 114B (collectively referred to as tin anodes 114), media column 116, pump 118, filter 120, pump 122, and rectifier 124, which is capable of generating the required current density. One or more cathodes 112 and one or more tin anodes 114 are positioned in tank 110. As shown in Figure 1, tin anodes 114 may be placed on either side of cathode 112. Tank 110 also contains an electrolytic solution containing tin, which has been described above. The electrolytic solution is circulated through media column 116 by pump 118 and is returned back to tank 110. Media column 116 contains an ion exchange resin. The flow rate through media column 116 is calculated to achieve a specified contact time between the electrolytic solution and the ion exchange resin. Adjusting the flow rate through media column 116 may vary the contact time. For example, increasing the flow rate of the electrolytic solution through media column 116 may decrease the contact time between the electrolytic solution and the ion exchange resin and conversely, decreasing the flow rate of the electrolytic solution through media column 116 may increase the contact time between the electrolytic solution and the ion exchange resin.

[0024] System 100 may also include filter 120. The electrolytic solution from tank 110 may be pumped through filter 120 by pump 122 and returned back to tank 110. Filter 120 may filter particulate matter from the solution. For example, filter 120 may remove material have a size greater than about 5 microns.

[0025] Rectifier 124 is connected to cathode 112 and anodes 114 and provides the required current density for dissolution of tin anodes 114 and electrodepositing tin from the electrolytic solution onto cathode 112 during the electrodepositing or electrorefining process. A suitable current density at the cathode may be as low as 10, 15, 20, 25, 30, 35, 40 amps per square foot (ASF) or as great as 25, 30, 35, 40, 45, 50, 55, 60, 65 or 70 ASF or may be within any range delimited by any pair of the foregoing values. In other embodiments, the current density at the cathode may be as low as 70, 80, 90, 100, 125 or 150 ASF or as great as 175, 200, 225, 250, 275 or 300 ASF or may be within any range delimited by any pair of the foregoing values. In one example, the current density was regulated at about 22 milliamps per square centimeter (mA/cm^2) (20 ASF) at cathode 112 and about 8-11 mA/cm^2 (7-10 ASF) at anodes 114.

[0026] The tin may be refined in a continuous process as described above. For example, the steps of exposing the electrolytic solution to an ion exchange resin and depositing the tin from the electrolytic solution onto a cathode may occur at least partially concurrently.

[0027] Alternatively, the tin may be refined in a step or batch process. For example, an electrolytic solution may be formed by electrolytic dissolution of tin anodes and a permeable membrane may be used to prevent tin from depositing on the cathode. The dissolution may then be stopped, and the electrolytic solution may be exposed to an ion exchange resin for a period of time. For example, the electrolytic solution may be passed through a column containing the ion exchange resin or the ion exchange resin may be added to the electrolytic solution tank. After exposure to the ion exchange resin, the electrolytic solution may be electrodeposited onto a cathode.

[0028] In some embodiments, the eletrorefining system may include two or more electrodeposition processes. Each electrodeposition process may include the same or different electrolytic solution compositions. For example, the electrolytic

solutions may include the same or different acids and/or additive(s) and/or have the same or different pH. One or more of the electrodeposition processes may including an ion exchange resin as described herein, and if present in two or more of the processes, the ion exchange resin may be the same or different. In some embodiments, two or more electrodeposition processes may be conducted in series or in succession such that tin ions are electrodeposited two or more times. For example, the electrorefining system may include electrodepositing tin ions from an electrolytic solution containing hydrochloric acid onto a cathode, electrolytic dissolution of the deposited tin into a second electrolytic solution containing sulfuric acid, and electrodepositing tin ions from the second electrolytic solution onto a second cathode. Impurities and/or contaminant components may be removed in each successive electrodeposition process. Further, different impurities and/or contaminant components may be removed based on the electrolytic solution composition and/or the ion exchange resin of the electrodeposition process.

[0029] In some embodiments, the electrorefined tin may not experience a significant reduction in lead content compared to that of the tin prior to the electrorefining process (e.g., the input or pre-refined tin). For example, the lead content may not be reduced by more than about 1% and particularly not by more than about 0.1% by the electrorefining process. A suitable lead content of the tin prior to the electrorefining process may be at least 1 ppm and more particularly at least about 2 ppm. A suitable lead content of the electrorefined tin may be at least about 1 ppm and more particularly at least about 2 ppm. In some embodiments, the lead content of the electrorefined tin may be as low as 0.01, 0.05 or 1.0 ppm or as great as 2.0, 5.0 or 10.0 ppm or may be within any range delimited by any pair of the foregoing values.

[0030] It has been found that electrodeposited tin which is produced by exposing the electrolytic solution to at least one ion exchange resin during electrorefining has reduced alpha particle emissions or alpha flux.

[0031] Although there is a relationship between a reduction in certain impurities such as thorium and a reduction in alpha particle emissions, a tin material having less than 1 ppm thorium will not necessarily have a sufficient low alpha particle emissions or alpha flux to satisfy certain industry requirements. For example

it is entirely possible to refine tin to a 6N purity level without reducing alpha particle emissions to a suitable level. Accordingly, in one example, electrorefined tin may be tested for alpha particle emissions after refining using, for example, a gas flow proportional counter such as an Alpha Sciences 1950 in the manner described in JEDEC standard JESD221.

[0032] The overall reduction in alpha particle emissions will vary depending on many factors including, but not limited to, the alpha particle emissions of the input or pre-refined tin material, the contact time of the electrolytic solution with the ion exchange resin, and the number of passes of the electrolytic solution through the ion exchange resin. In one example, the alpha particle emissions of the refined tin material is reduced by at least 50%, more particularly at least 75%, and even more particularly at least 85%, 90% or 95% compared to the alpha particle emissions of the same material prior to deposition of the electrorefined tin. In another example, electrorefining is carried out under conditions suitable to reduce the alpha particle emissions of the refined tin material to less than about 0.01 counts/hour/cm², more particularly less than about 0.002 counts/ hour/cm², and even more particularly less than about 0.001 counts/hour/cm².

[0033] It should be noted that the alpha particle emissions of tin does not necessarily remain stable after the material has been refined. In particular, alpha particle emissions or alpha flux of the refined tin may increase or decrease over time due to the residual presence and radioactive decay of various elements such as ²¹⁰Pb. The increase or decrease of alpha particle emissions over time may be referred to as alpha drift.

[0034] As described herein, it has surprisingly been found that not only does the electrorefining process including an ion exchange resin reduce the alpha particle emissions of the electrorefined tin immediately after the electrorefining process but it also results in reduced alpha drift and reduces the alpha particle emissions at a period of time after the electrorefining process. In one embodiment, the alpha particle emissions of the refined tin 90 days after the electrorefining process is at least 50%, more particularly at least 75%, and even more particularly at least 85%, 90% or 95% less than the alpha particle emissions of the same material prior to electrorefining. In another example, the electrorefining is carried out under conditions

suitable to reduce the alpha particle emissions of the electrorefined tin to less than about 0.01 counts/hour/cm², more particularly less than about 0.002 counts/hour/cm² and even more particularly less than about 0.001 counts/hour/cm², when measured 90 days after the electrorefining process.

II. Method of Determining the Alpha Particle Emission Potential of Electrorefined Tin.

[0035] A method for determining the alpha particle emission potential of the electrorefined tin, such as the maximum alpha particle emissions from the tin, is described herein. The described method, for example, can be used to predict or forecast the maximum alpha particle emissions from the tin.

[0036] As used herein, the term "target parent isotope" refers to an isotope of interest which is present in a metallic material and is able to decay to a daughter isotope, wherein the daughter isotope may subsequently alpha-decay, i.e., may decay to a further isotope with concomitant emission of an alpha particle. The term "target decay isotope", as used herein, refers to an isotope of interest which is a daughter isotope of the target parent isotope and itself may subsequently alpha-decay, i.e., may decay to a further isotope with concomitant emission of an alpha particle. The target decay isotope may or may not be itself a direct decay product of the target parent isotope. For example, if ²¹⁰Pb is a target parent isotope, ²¹⁰Po may be a target decay isotope even though ²¹⁰Pb decays to ²¹⁰Bi with subsequent decay of ²¹⁰Bi to ²¹⁰Po.

[0037] According to the present method, the metallic material (e.g., tin) is subjected to a secular equilibrium disruption process. As used herein, the term "secular equilibrium disruption process" refers to a process to which the metallic material is subjected which at least partially disrupts the secular equilibrium of the decay profile of at least one target parent isotope within the metallic material. In most instances, the secular equilibrium disruption process disrupts the secular equilibrium of the decay profile of a target parent isotope by reducing the concentration of the target parent isotope in the metallic material, by reducing the concentration of a corresponding target decay isotope in the metallic material, or by a combination of the foregoing. The electrorefining process described herein is an

exemplary secular equilibrium disruption process. Other exemplary secular equilibrium disruption processes include melting, casting, smelting, refining (such as electro-chemical refining, chemical refining, zone refining, and vacuum distillation). A secular equilibrium disruption process may also include any combination of two or more of the foregoing processes. Typically, in the secular equilibrium disruption process, and particularly when the secular equilibrium disruption process is at least in part a refining process, both the target parent isotopes and the target decay isotopes are at least partially removed as impurities by physical and/or chemical separation from the bulk metallic material.

[0038] In some embodiments, the secular equilibrium disruption process may remove substantially all of a given target decay isotope and thereby effectively "reset" the secular equilibrium of the corresponding target parent isotope. For example, in the case of a metallic material including ^{210}Pb as a target parent isotope, the secular equilibrium disruption process may substantially completely remove all of the ^{210}Po target decay isotope in the material, such that the secular equilibrium of ^{210}Pb is effectively reset, wherein substantially all ^{210}Po that is present in the material following the secular equilibrium disruption process is generated by decay of ^{210}Pb after the said disruption process. However, the present process may also be practiced using secular equilibrium disruption processes that remove only a portion of the target parent isotope and/or target decay isotope, and the present process is not limited to secular equilibrium disruption processes that remove substantially all of a given target decay isotope.

[0039] In some embodiments, the secular equilibrium disruption process may be completed in a relatively short amount of time and, in other embodiments, the secular equilibrium disruption processes may require a relatively greater amount of time for completion, depending on the nature of the process and the number of processes that together may constitute the secular equilibrium disruption process. Therefore, the elapsed time discussed below, between the secular equilibrium disruption process and the measurement of alpha particle emissions of the metallic material, may be an elapsed time between the completion of the secular equilibrium disruption process (or processes) and the measurement of alpha particle emissions of the metallic material.

[0040] After the metallic material (e.g., tin) is subjected to the secular equilibrium disruption process, the alpha particle emission of the metallic material is detected, i.e., an alpha particle emission measurement is obtained. Although it is within the scope of the present disclosure to obtain an alpha particle emission of the entire metallic material in bulk form, typically a sample of the bulk metallic material will be obtained for purposes of alpha particle emission analysis.

[0041] A relatively thin portion of the bulk metallic material may be obtained as a sample by a suitable method such as rolling the bulk metallic material to provide a thin sheet of sample material, or by any other another suitable method.

[0042] After the sample is obtained, the sample is treated by heat in order to promote diffusion of target decay isotopes in the sample material until such point that the concentration of atoms of the target decay isotopes in the sample is uniform throughout the sample volume. In many samples, there may be a larger concentration of atoms of target decay isotopes toward the center of the sample, for example, or otherwise in other areas of the sample such that a concentration mismatch or gradient is present. The heat treatment removes any such concentration mismatches or gradients by promoting diffusion of atoms of target decay isotopes within the sample from areas of relatively higher concentration toward areas of relatively lower concentration such that a uniform concentration of target decay isotopes is obtained within the sample. When such uniform concentration is obtained, the number of atoms of target decay isotopes within a detection limit depth of the alpha particle detection process will be representative of and, more particularly will correlate directly to, the uniform concentration of atoms of target decay isotopes in the entirety of the sample. Such uniform concentration is achieved when the chemical potential gradient of the target decay isotopes is substantially zero and the concentration of the target decay isotopes is substantially uniform throughout the sample.

[0043] Stated in another way, at room temperature, the test sample may have a chemical potential gradient, in that the concentration of target decay isotopes is higher on one side of the sample than another side of the sample, or at the centroid of the sample than at the outer surfaces of the sample. Heating of the sample adjusts the chemical potential gradient and, at a sufficient time and temperature

exposure, the chemical potential gradient is substantially zero and the concentration of the target decay isotopes is substantially uniform throughout the sample.

[0044] As used herein, the term "detection limit depth" refers to a distance within a given metallic material through which an emitted alpha particle may penetrate in order to reach a surface of the material and thereby be released from the material for analytical detection. Detection limit depths for ^{210}Po in selected metallic materials are provided in Table 2 below, in microns, which is based on the penetration of the 5.304 MeV alpha particle released upon decay of ^{210}Po to ^{206}Pb :

Table 2
Detection limit depths of ^{210}Po in selected metallic materials

<i>Metallic material</i>	<i>Detection limit depth of ^{210}Po (microns)</i>
Tin (Sn)	16.5
Aluminum (Al)	23.3
Copper (Cu)	11
Bismuth (Bi)	17.1

[0045] The detection limit depth for alpha particles of differing energy, such as alpha particles emitted upon radioactive decay of alpha particle-emitting isotopes other than ^{210}Po , will vary, with the detection limit depth generally proportional to the energy of the alpha particle. In the present method, emitted alpha particles may be detected by use of a gas flow counter such as an XIA 1800-UltraLo gas ionization chamber available from XIA L.L.C. of Hayward, CA according the method described by JEDEC standard JESD 221.

[0046] Target decay isotopes such as ^{210}Po are known to diffuse or migrate within metallic materials and, in this respect, the heat treatment of the present method is used to promote diffusion of the target decay isotope within the material sample to eliminate concentration gradients. In particular, target decay isotopes, such as ^{210}Po , will have a diffusion rate J in a given metallic material, which can be expressed according to equation (1) below:

$$J = -D \frac{\partial \phi_{Po}}{\partial x} \quad (1)$$

wherein:

$\partial \Phi / \partial x$ is the concentration gradient of the target decay isotope, such as ^{210}Po ; and D is the diffusion coefficient.

[0047] The concentration gradient of the target decay isotope is determined by measuring the alpha particle emissions at the surface of a sample, removing a layer of material of x thickness, such as by chemical etching, and measuring the alpha particle emissions at the x depth. The concentration of the target decay isotope at the original surface and at depth x is directly proportional to the alpha particle emission at each surface, and concentration gradient of the target decay isotope is calculated as the difference between the concentration at one of the surfaces and the concentration at depth x over the distance x .

[0048] To determine the polonium diffusion rate J , the polonium alpha particle emissions from 5-5.5 MeV in a tin sample was measured. The sample was then heated at 200 °C for 6 hours, and the alpha particle emission measurement was repeated. The number of polonium atoms N is calculated from equation (2) below:

$$N = A / \lambda_{Po} \quad (2)$$

wherein:

A is the alpha particle emission measured in counts/hr; and

$\lambda_{Po} = \ln 2 / 138.4$ days, based on the half-life of ^{210}Po .

[0049] The number of moles of polonium calculated by dividing the number of polonium atoms N by Avogadro's number. Dividing the difference in the number of moles of polonium by the sample area (0.1800 m^2) and the time over which the sample was heated (6 hours) yields a lower bound on the diffusion rate of $4.5 \times 10^{-23} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ at 473K in tin.

Table 3
Data for diffusion rate determination

Measurement	A (Counts/Hr)	N (atoms)	Moles
Initial	24.75	1.19E+05	1.97E-19
Final	46.71	2.24E+05	3.72E-19

[0050] Based on equation (1), one may determine a suitable time and temperature heating profile to which the sample may be exposed in order to diffuse the target decay isotope within the sample sufficiently to eliminate any concentration gradients, such that detection of alpha particle emissions within the detection limit depth of the sample is representative, and directly correlates, to the concentration of the target decay isotope throughout the sample. For example, for a tin sample having a thickness of 1 millimeter, a heat treatment of 200 °C for 6 hours will ensure that any concentration gradients of ^{210}Po atoms within the sample are eliminated.

[0051] Thus, for a given metallic material and sample size, the application of heat may be selected and controlled by time and temperature exposure of the sample to ensure that atoms of a target decay isotope are diffused to a sufficient extent to eliminate concentration gradients. It has been found that, by the present method, in providing a suitable time and temperature profile for the heat treatment step, measurement of alpha particle emissions from a target decay isotope present within the detection limit depth directly corresponds to the concentration or number of target decay isotope atoms within the entirety of the sample.

[0052] It is generally known that subjecting a metallic material to heat promotes diffusion of elements within the material. However, prior methods have employed heat treatment simply to increase the number of alpha particle emissions detected over background levels to thereby increase the signal to noise ratio of the alpha particle emission detection.

[0053] The alpha particle emissions attributable to ^{210}Po is expressed as polonium alpha activity, A_{Po} , at a time (t) following the secular equilibrium disruption process. From the A_{Po} and elapsed time (t), the concentration of ^{210}Pb atoms in the sample can be calculated using equation (3):

$$[^{210}\text{Pb}]_0 = \frac{\lambda_{Po} - \lambda_{Pb}}{\lambda_{Po}\lambda_{Pb}(e^{-\lambda_{Pb}t} - e^{-\lambda_{Po}t})} (A_{Po}(t) + A_{Po}(t_0)e^{-\lambda_{Po}t})$$

(3)

wherein:

λ_{Po} = $\ln 2/138.4$ days, based on the half-life of ^{210}Po ;

λ_{Pb} = $\ln 2/22.3$ years (8,145.25 days) based on the half-life of ^{210}Pb ; and

time (t) is the time which has elapsed between the secular equilibrium disruption process and the alpha particle emission measurement.

[0054] Due to the fact that ^{210}Pb has a 22.3 year half-life, the ^{210}Pb concentration is substantially constant over the time (t), particularly when the time (t) is less than three years,. Also, when substantially all of the ^{210}Po is removed in the secular equilibrium disruption process (which may be the case when the secular equilibrium disruption process is a strenuous refining process, for example) the last term in equation (3) above is very near to zero because the initial ^{210}Po concentration will be very near to zero when the alpha particle emissions are measured relatively soon after the secular equilibrium disruption.

[0055] The concentration of the target parent isotope may be calculated by the above-equation (3) and, once the concentration of the target parent isotope is calculated, the known half-life of the target parent isotope may be used to provide an assessment or prediction of a maximum concentration of the target decay isotope within the material based on the re-establishment of the secular equilibrium profile of the target parent isotope.

[0056] In other words, once the concentration of ^{210}Pb atoms is determined using equation (3), based on the half-life of ^{210}Pb the maximum ^{210}Po activity at re-establishment of secular equilibrium will occur at (t)=828 days, and is calculated from equation (4) below:

$$A_{Po}(t=828d) = \frac{\lambda_{Pb}\lambda_{Po}}{\lambda_{Po} - \lambda_{Pb}} [^{210}\text{Pb}]_0 (e^{-\lambda_{Pb}828d} - e^{-\lambda_{Po}828d}) \quad (4)$$

[0057] Consistent time units (i.e., days or years) should be used across equation (3) and equation (4).

[0058] The maximum ^{210}Po activity directly correlates to a maximum alpha particle emission of the material, and will occur at 828 days from the secular equilibrium disruption process. In this manner, due to the fact that the present method will typically be carried out relatively soon after the secular equilibrium disruption process, the calculated maximum concentration of the target decay isotope and concomitant alpha particle emission will typically be a maximum future concentration of the target decay isotope and concomitant alpha particle emission that the metallic material will exhibit over a timeframe which corresponds to the half-life of the target parent isotope.

[0059] For example, based on the half-life of ^{210}Pb , the applicable timeframe or "window" by which a maximum possible concentration of ^{210}Po (and thereby a peak in alpha particle emissions) will be reached in the material will occur at 828 days (27 months) from the secular equilibrium disruption process.

[0060] It is also possible to calculate a possible concentration of ^{210}Po (and thereby the alpha particle emissions) at any specified elapsed time from the secular equilibrium disruption process. In this manner, it is possible to calculate a possible concentration of ^{210}Po after a sufficient elapsed time from the secular equilibrium disruption process, where the sufficient elapsed time may be at least 200, 250, 300, 350 or 365 days from the secular equilibrium disruption process. For example, based on the half-life of ^{210}Pb , the applicable timeframe by which the ^{210}Po concentration will reach 67% of the maximum possible concentration in the material will occur at 200 days from the secular equilibrium disruption process. Similarly, the ^{210}Po concentration will reach 80% and 88% of the maximum possible concentration in the material at 300 days and 365 days, respectively, from the secular equilibrium disruption process.

[0061] Advantageously, according to the present method, after a metallic material has been subjected to a secular equilibrium disruption process such as by refining the metallic material, a maximum alpha particle emission that the metallic material will reach during the useful life of the material may be accurately predicted. In this manner, the present method provides a valuable prediction of the maximum alpha

particle emission for metallic materials, such as solders, that are incorporated into electronic devices.

III. Examples

[0062] The present invention is more particularly described in the following examples that are intended as illustration only, since numerous modifications and variations within the scope of the present invention will be apparent to those skilled in the art. Unless otherwise noted all parts, percentages and ratios reported in the following examples are on a volume basis, and all reagents used in examples were obtained, or are available, from the chemicals suppliers described below, or may be synthesized by conventional techniques.

Example 1

Inclusion of ion exchange resin in an electrorefining process

Materials Used

[0063] Monophos resin: an ion exchange resin having sulfonated and phosphomethylated functional groups and available from Eichrom.

[0064] Lewatit MonoPlus TP 260: an ion exchange resin having amino methyl phosphonic acid functional groups and available from Lanxess.

[0065] Reillex HPQ Polymer: an ion exchange resin having poly(4-vinyl-pyridine) functional groups and available from Vertellus.

Electrorefining Process

[0066] An electrolytic solution was added to a 30 liter (L) polypropylene tank equipped with a vertical pump for solution agitation and filtration. A central titanium cathode and two 4N tin anodes (one on each side of the cathode) were positioned in the tank, and a DC power supply was connected to the cathode and anodes for generating the required current density. During the electrorefining process, the DC current passing between the cathode and anodes was regulated to 22 mA/cm² (20 ASF) at the cathode and 8-11 mA/cm² (7-10 ASF) at each anode.

[0067] An ion exchange resin was prewashed with at least 10 bed volumes of deionized water and placed in a glass column. The glass column had a diameter of

approximately 1 inch and contained approximately 77.0 cubic centimeters (4.7 cubic inches) of the ion exchange resin. The electrolytic solution was continuously circulated through the glass column by a magnetically coupled 1/250 HP Iwaki pump during the electrorefining process at a flow rate between 100 and 500 mL per minute.

[0068] The tin was electrorefined for three days, and then harvested from the cathode. The harvested tin was rinsed for five minutes with deionized water having a purity of 5 megaohms per centimeter. The electrorefined tin was then dried for 15 minutes at 150°C, and cast at 300°C-350°C. Three crops were harvested for each example. A sample was taken from each crop, and analyzed by an Alpha Sciences 1950 alpha counter in the manner described in JEDEC standard JESD221 and a Varian Vista Pro inductive coupled plasma atomic emission spectroscopy (ICP-AES) for trace elements.

Control

[0069] The Control did not include an ion exchange resin in the electrorefining process. A sulfuric acid electrolyte was formed by mixing 3% sulfuric acid by volume with deionized water. Tin from the anodes was electrolytically dissolved from high purity tin anodes in the sulfuric acid electrolyte to form a 15 g/L solution. Technistan Antioxidant (an antioxidant) was added at a volume percent of 1% by volume of the total electrolytic solution and Technistan TP-5000 additive (an organic grain refiner) was added at a volume percent of 4% by volume of the total electrolytic solution. The electrolytic solution had a pH of less than about 1 (calculated pH).

[0070] Electrolysis was performed at 20°C using a cathode current density of 22 mA/cm² (20 ASF). The cathodes were harvested after 72 hours. The tin was cast. The casts were analyzed by the Alpha Sciences 1950 alpha counter (in the manner described in JEDEC standard JESD221) and the Varian Vista Pro ICP-AES. The mean alpha particle emissions (in counts/hour/cm²) and standard deviation ("SD") based on three samples are shown in Table 4 as measured immediately after casting ("refined alpha") and after storage for at least 90 days ("alpha after 90 days").

Table 4
Refined tin sample data

Starting alpha		Refined alpha			Alpha after 90 days		
Mean	SD	Mean	SD	Percent reduction	Mean	SD	Percent reduction
0.0119	0.0080	0.0005	0.008	96%	0.0068	0.00046	15%

[0071] The electrorefining process of the Control, which did not include an ion exchange resin, reduced the alpha particle emissions by 96% immediately following the refining process. However, the alpha particle emissions or alpha flux increased after 90 days, resulting in an alpha reduction of only 15%.

Samples 1-3

[0072] Samples 1-3 included an ion exchange resin in the electrorefining process. An electrolytic solution containing sulfuric acid, deionized water, tin, Technistan Antioxidant and Technistan TP-5000 was prepared as described above for the Control.

[0073] Electrolysis was performed at 20°C using a cathodic current density of 22 mA/cm² (20 ASF). Electrolytic solution from the main tank was pumped through the glass column which contained the designated ion exchange resin at the designated flow rate. The ion exchange resin and flow rates are presented in Table 5.

Table 5
Electrorefining process information

	<i>Ion Exchange Resin</i>	<i>Flow Rate</i>	
Sample 1	Monophos	450	ml/min
Sample 2	Lewatit MonoPlus TP 260	320	ml/min
Sample 3	Reillex HPQ Polymer	210	ml/min

[0074] The cathodes were harvested after 72 hours from the start of the electrorefining process. The electrorefined tin was cast, and the casts were analyzed by the Alpha Sciences 1950 alpha counter (in the manner described in JEDEC standard JESD221) and the Varian Vista Pro ICP-AES. The mean alpha particle emissions (counts/hour/cm²) and standard deviation ("SD") for three samples as measured immediately after casting ("refined alpha") and at least 90 days after

casting ("alpha after 90 days") are shown in Table 6. The percent reduction ("% reduct.") of mean alpha particle emissions based on the starting alpha particle emissions is also shown.

Table 6
Refined tin alpha emissivity data

<i>Sample</i>	<i>Starting alpha</i>		<i>Refined alpha</i>			<i>Alpha after 90 days</i>		
	<i>Mean</i>	<i>SD</i>	<i>Mean</i>	<i>SD</i>	<i>% Reduct.</i>	<i>Mean</i>	<i>SD</i>	<i>% Reduct.</i>
1	0.0043	0.0018	0.0002	0	95	0.0005	0.0005	88
2	0.0054	0.0016	0.0001	0.0001	99	0.0007	0.0006	88
3	0.0052	0.0020	0.0001	0.0001	98	0.0005	0.0002	90

[0075] Alpha particle emissions of Samples 1-3 immediately after refining and casting were similar to that of the control. Ninety (90) days after casting, the alpha particle emissions of Samples 1-3 were significantly reduced compared to the control.

[0076] The lead content of the samples were analyzed before and after electrorefining by Varian Vista Pro ICP-AES. The lead content for Samples 1-3 are provided in Table 7.

Table 7
Refined tin lead content data

	<i>Lot</i>	<i>Starting Pb (ppm)</i>	<i>Refined Pb (ppm)</i>
Sample 1	1	5	5
	2	5	5
	3	4	5
Sample 2	1	4	5
	2	4	4
	3	4	4
Sample 3	1	4	4
	2	4	4
	3	4	4

[0077] Electrorefining did not significantly change the lead content in Samples 1-3. Further, any measured change in lead content is within the experimental margin of error.

Samples 4-20

[0078] Samples 4-20 included an ion exchange resin in the electrorefining process. An electrolytic solution containing sulfuric acid, deionized water, tin, Technistan antioxidant and Technistan TP-5000 was prepared as described above for the Control.

[0079] Electrolysis was performed at 20°C using a cathodic current density of 22 mA/cm² (20 ASF). Electrolytic solution from the main tank was pumped through the glass column which contained the designated ion exchange resin at the designated flow rate. The ion exchange resin, flow rates (mL/min), alpha particle emissions (counts/hour/cm²), including mean and standard deviation ("SD") are presented in Table 8.

Table 8
Refined tin sample data

<i>Sample</i>	<i>Ion Exchange Resin</i>	<i>Flow Rate</i>	<i>Starting alpha</i>		<i>Refined alpha</i>		
			<i>Mean</i>	<i>SD</i>	<i>Mean</i>	<i>SD</i>	<i>Percent reduction</i>
4	Dowex G-26	280	0.003	0.0005	0.0004	0.0001	87%
5	Dowex Optipore L493	227	0.003	0.0005	0.0006	0.0003	79%
6	Dowex MAC-3	3.8	0.003	0.0005	0.0006	0.0004	80%
7	Amberlite IRC-747	3.6	0.003	0.0005	0.0003	0.0001	90%
8	Diphonix resin	355	0.003	0.0005	0.0009	0.0015	69%
9	Amberlyst A-26	240	0.003	0.0005	0.0017	0.0013	44%
10	Dowex PSR-2	260	0.003	0.0005	0.0003	0.0003	91%
11	Amberlyst 15WET	400	0.003	0.0005	0.0006	0.0006	79%
12	Lewatit TP-260	235	0.00413	0.00196	0.0000	0.0000	100%
13	XZ 91419.00 resin	285	0.00413	0.00196	0.0005	0.0005	88%
14	Lewatit TP-207	235	0.00413	0.00196	0.0001	0.0001	97%
15	XUS 43568 resin	320	0.00413	0.00196	0.0001	0.0001	98%
16	Amberlite PWA 5	400	0.00640	0.0005	0.0005	0.0005	93%

17	Dowex 21K XLT	240	0.00640	0.0005	0.0005	0.0004	92%
18	Dowex G-26	210	0.00640	0.0001	0.0004	0.0001	94%
19	Amberlite IRC 747	430	0.00640	0.0001	0.0008	0.0001	88%
20	Reillex HP	250	0.00640	0.0001	0.0009	0.0001	85%

[0080] The alpha particle emissions were reduced the greatest amount in Sample 12 (100%), which included Lewatit TP-260 ion exchange resin and was reduced the least in Sample 9 (44%).

[0081] The lead content of the samples were analyzed before (e.g., pre-refining) and after (e.g., post-refining) electrorefining by the Varian Vista Pro ICP-AES. Three samples, or lots, were analyzed for each resin tested. The lead content for Samples 4-20 are provided in Table 9.

Table 9
Refined tin sample lead content data

Sample	Lot	Starting Pb (ppm)	Refined Pb (ppm)
4	1	5	6
	2	5	5
	3	5	4
5	1	5	5
	2	5	6
	3	5	4
6	1	5	5
	2	5	5
	3	5	5
7	1	5	6
	2	5	5
	3	5	4
8	1	5	5
	2	5	5
	3	5	4
9	1	5	5
	2	5	4
	3	5	4

10	1	5	5
	2	5	5
	3	5	4
11	1	5	5
	2	5	5
	3	5	4
12	1	5	6
	2	5	5
	3	4	5
13	1	5	5
	2	5	5
	3	4	4
14	1	5	5
	2	5	5
	3	4	5
15	1	5	6
	2	5	5
	3	4	5
16	1	4	5
	2	4	5
	3	4	5
17	1	4	6
	2	4	5
	3	4	5
18	1	4	5
	2	4	5
	3	4	5
19	1	4	5
	2	4	5
	3	4	5
20	1	4	5
	2	4	5
	3	4	3

[0082] Electrorefining did not significantly change the lead content in Samples 4-20.

Example 2

Adjustment of tin concentration and current density in an electrorefining process

[0083] The effects of tin concentration and current density were investigated in Samples 21-25. Electrolytic solutions containing sulfuric acid, deionized water, tin, Technistan Antioxidant and Technistan TP-5000 were prepared as described above for the Control.

[0084] During the electrodeposition process, the electrolytic solution from the main tank was pumped through the glass column containing Lewatit MonoPlus TP 260 ion exchange resin. The tin was deposited at 20°C and onto a cathode having an active area of 72 square inches. The tin concentration of the electrolytic solution, the cathodic current in amps and the cathodic current density in ASF for each sample is provided in Table 10.

Table 10
Electrorefining process information

Sample	<i>Tin concentration (g/L)</i>	<i>Current (Amps)</i>	<i>Current density (ASF)</i>
21	20	5	10
22	40	15	30
23	20	25	50
24	60	5	10
25	60	25	50

[0085] Before the electrorefining process, the input or pre-refined tin had alpha particle emissions of 0.048 counts/hour/cm². The post-refined alpha particle emissions and elapsed time between refining and the measurement of alpha particle emissions are shown below in Table 11. The alpha particle emissions were measured at multiple elapsed times for select samples.

[0086] Table 11 also includes percent reduction and the reduction factor of the measured alpha particle emissions as compared to the input or pre-refined alpha particle emissions. The percent reduction was calculated by the difference between the pre-refined and post-refined alpha particle emissions divided by the pre-refined alpha particle emissions. The reduction factor was calculated by the pre-refined alpha particle emissions divided by the post-refined alpha particle emissions.

Table 11

Refined tin sample alpha emissivity data

Sample	Lot	Alpha particle emissions (counts/hr/cm2)	Elapse time (days)	Percent reduction	Reduction factor
21	1	0.02	26	58%	2.4
	2	0.0138	23	71%	3.5
	3	0.009	21	81%	5.3
	3	0.021	47	56%	2.3
22	1	0.0137	13	71%	3.5
	1	0.026	39	46%	1.8
	2	0.012	9	75%	4.0
	3	0.0103	6	79%	4.7
23	1	0.0136	19	72%	3.5
	2	0.0094	16	80%	5.1
	3	0.0095	10	80%	5.1
	3	0.0301	39	37.3%	1.6
24	1	0.013	35	73%	3.7
	1	0.024	54	50.0%	2.0
	2	0.0093	27	81%	5.2
	3	0.0058	20	88%	8.3
25	1	0.0029	14	94%	16.6
	1	0.0088	34	81.7%	5.5
	2	0.0035	14	93%	13.7
	3	0.0016	13	97%	30.0
	3	0.0093	34	81%	5.2

[0087] Sample 21, which had the lowest tin concentration and the lowest current density, provided the least reduction in alpha particle emissions. Sample 25, which had the highest tin concentration and the highest current density, provided the greatest reduction in alpha particle emissions.

[0088] A plot of the alpha particle emissions over time for each sample is provided in Figure 2. A linear trend line was fit to each data set, and the equations are presented in Figure 2. The linear trend line for Sample 22 had a slope of 0.0005, Sample 23 had a slope of 0.0008, Sample 24 had a slope of 0.0005 and Sample 25 had a slope of 0.0003. A linear trend line could not be fit to the data for Sample 21.

Example 3

Determination of maximum alpha emissions in refined tin samples

[0089] The present method was used to assess the maximum potential alpha emissions in eight refined tin samples. The tin samples were refined according to the method described herein. Test samples of the refined tin samples were obtained by cutting an approximately 1 kilogram sample from an ingot and rolling the sample to a thickness of 1 millimeter. The test samples were heated at 200°C for six hours, and the alpha particle emissions of the test samples were measured using an XIA 1800-UltraLo gas ionization chamber available from XIA L.L.C. of Hayward, CA. The measured alpha particle emissions and elapsed times between refining and the measurement of alpha particle emissions are shown below in Table 12.

Table 12
Refined tin sample data

Sample	Alpha particle emissions (alpha flux) (counts/hr/cm²)	Elapsed time (t) between refining and measurement of alpha particle emissions (days)	²¹⁰Pb concentration at time=0 (atoms/cm²) (equation (2))	Maximum alpha particle emission (equation (3))
26	0.002	89	66	0.0056
27	0.0045	258	74	0.0063
28	0.0016	113	44	0.0037
29	0.004	272	64	0.0055
30	0.0016	211	29	0.0025
31	0.0009	32	72	0.0061
32	0.025	553	324	0.0276
33	0.0195	523	255	0.0217

[0090] From the measured alpha particle emission and the elapsed time (t) between refining and the measurement of alpha particle emission, the concentration of ²¹⁰Pb at (t)=0 can be calculated from equation (3) above.

[0091] For example, the alpha particle emission of Sample 26 was measured at 0.002 counts/hr/cm² at 89 days from refining. Based on equation (3) above, the number of ²¹⁰Pb atoms per cm² ([²¹⁰Pb]₀) needed to generate the measured ²¹⁰Po activity, i.e., measured alpha particle emission, was calculated to be 66. Using equation (4) above, the activity or predicted alpha particle emission of ²¹⁰Po at (t)=828 days was calculated as 0.0056 counts/hr/cm².

[0092] In Sample 32, the alpha particle emission was measured at 0.025 counts/hr/cm² at 523 days from refining. The value of [²¹⁰Pb]₀ was calculated based on equation (3) to be 255 atoms/cm², and the maximum alpha particle emission was calculated based on equation (4) as 0.0217 counts/hr/cm².

[0093] As may be seen from Samples 26 and 32, the difference between the measured alpha particle emission and the calculated maximum alpha particle emission decreases as time (t) approaches 828 days, with the greater difference for Sample 26 attributable to the alpha particle emission measurement being obtained early in the secular equilibrium cycle (e.g., less time had elapsed from the secular equilibrium disruption event) before secular equilibrium could be re-established after refining.

Example 4

Determination of time required to diffuse the target decay isotope

[0094] The time required to diffuse the target decay isotope in a tin sample was investigated. Tin samples were refined according to the method disclosed herein. A test sample of the refined tin sample was obtained by cutting a sample from an ingot and rolling the sample to a thickness of 0.45 millimeter. The test sample was heated at 200°C for one hour, and the alpha particle emissions of the test samples were measured using an XIA 1800-UltraLo gas ionization chamber available from XIA L.L.C. of Hayward, CA. Measurement of the alpha particle emissions required about 24 hours, after which the sample was heated for one hour at 200°C and then measured for alpha particle emissions. This process (e.g., heat for one hour followed by measurement of alpha particle emissions) was repeated for a total of five heat/measurement cycles. The measured alpha particle emissions and the total hours the sample was heated at 200°C are shown below in Table 13.

Table 13

Refined tin sample data

<i>Total hour(s) sample heated</i>	<i>Alpha particle emissions (alpha flux) (counts/hr/cm²)</i>
0	0.017
1	0.025
2	0.024
3	0.027
4	0.025
5	0.026

[0095] As can be seen from Table 13, the activity or alpha flux of the sample increased from 0.017 counts/hr/cm² to 0.025 counts/hr/cm² after one hour at 200C. That is, the activity or alpha flux of the tin sample increased more than 50% after one hour at 200°C. As further shown in Table 13, there was no significant change in the activity or alpha flux of the sample when heated for more than one hour at 200°C, suggesting that one hour at 200°C was sufficient to achieve a substantially uniform concentration of the target decay isotopes throughout the sample.

[0096] Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

[0097] In the foregoing, all temperatures are set forth uncorrected in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

[0098] From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

WHAT IS CLAIMED IS:

1. A method for purifying tin, the method comprising:
exposing an electrolytic solution comprising tin to an ion exchange resin; and
depositing electrorefined tin from the electrolytic solution.
2. The method of claim 1, wherein the electrorefined tin has alpha particle emissions of less than about 0.01 counts/hour/cm².
3. The method of claim 1, wherein the exposing and depositing steps occur at least partially concurrently.
4. The method of claim 1, wherein the ion exchange resin comprises functionalized carboxylic acid from the phosphonic acids group.
5. The method of claim 1, wherein the ion exchange resin comprises phosphomethylated functional groups.
6. The method of claim 1, wherein the ion exchange resin comprises amino methyl phosphonic acid functional groups.
7. The method of claim 1, wherein the ion exchange resin comprises poly(4-vinyl-pyridine) functional groups.
8. The method of claim 1, wherein at least 90 days after the deposition step, the electrorefined tin has an alpha particle emissions of less than about 0.01 counts/hour/cm².
9. The method of claim 1 and further comprising:
detecting alpha particle emissions from a sample of the deposited electrorefined tin;
determining a concentration of a target parent isotope in the sample of the deposited electrorefined tin from the alpha particle emissions detected in said detecting step and a time which has elapsed between said detecting step and said exposing and depositing steps; and

determining an alpha emission potential of a target decay isotope of the target parent isotope from the determined concentration of the target parent isotope and the half-life of the target parent isotope.

10. The method of claim 1, wherein at least 90 days after the step of depositing, the electrorefined tin has an alpha particle emissions that is at least 75% less than the alpha particle emissions of the tin prior to the exposing and depositing steps.

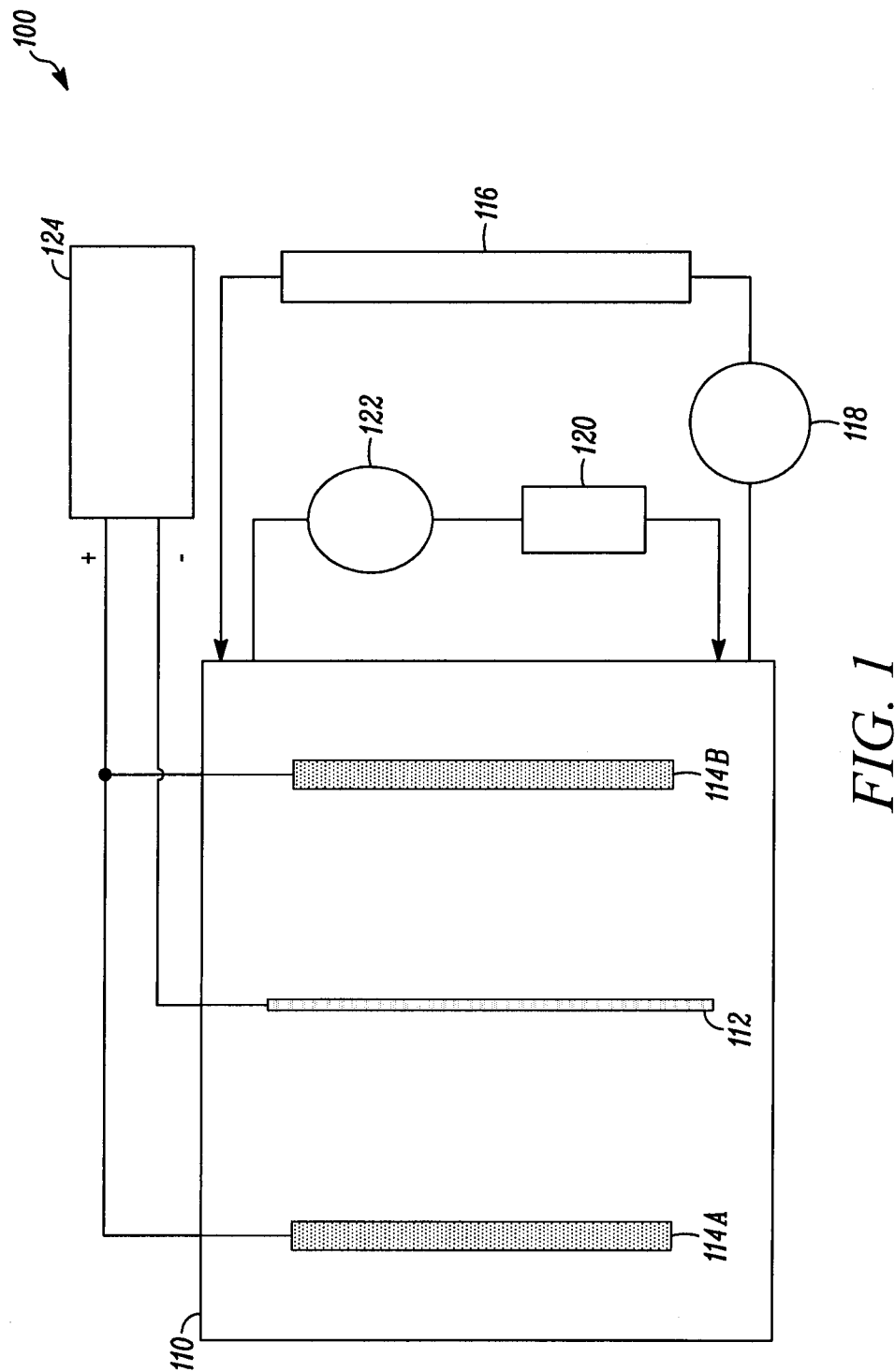


FIG. 1

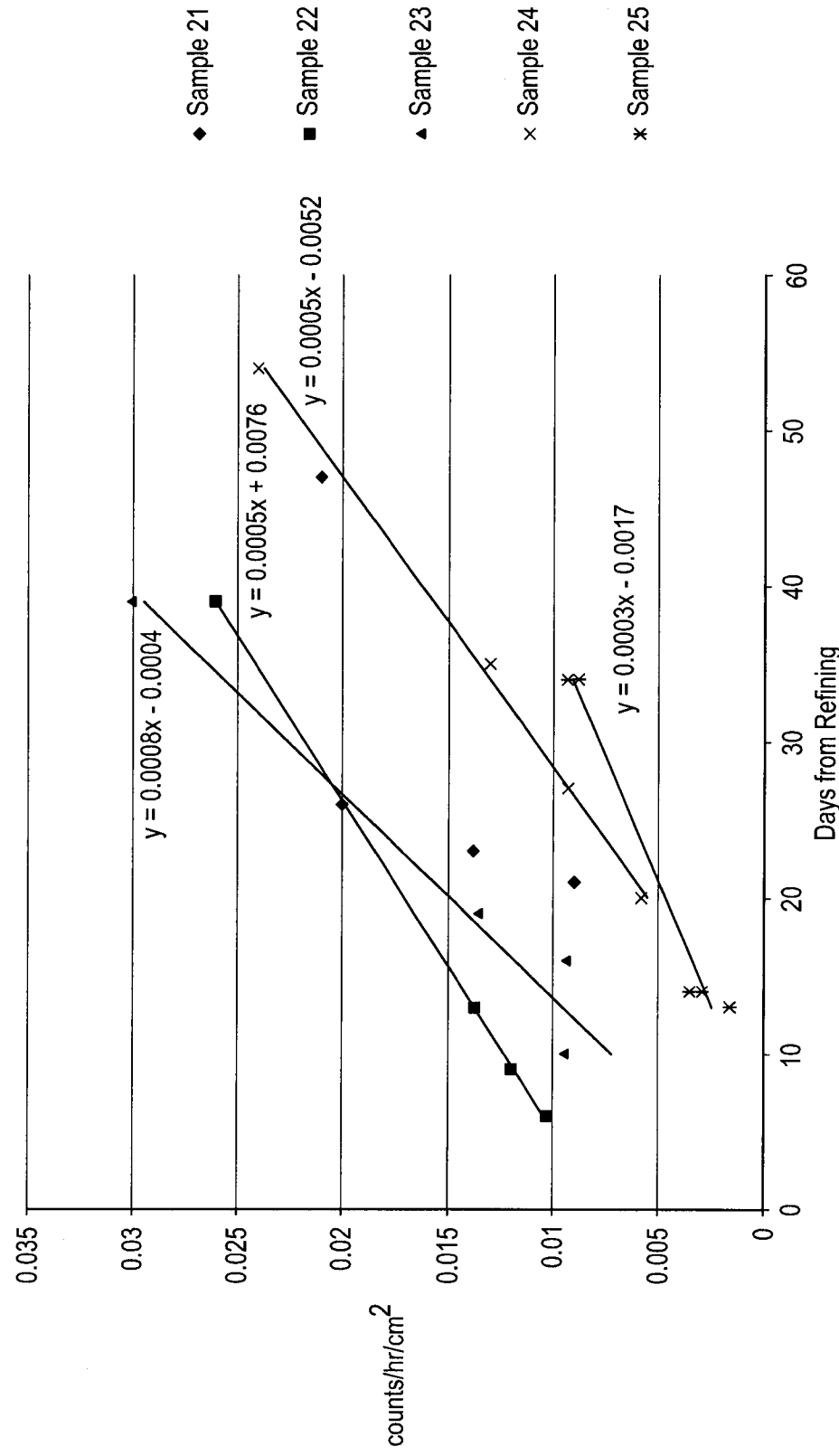


FIG. 2

A. CLASSIFICATION OF SUBJECT MATTER**H01L 21/306(2006.01)i, H01L 21/302(2006.01)i**

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)

H01L 21/306; B23K 35/22; C25C 1/14; C25C 1/00; C22B 25/06; H01L 23/48; C22C 13/02; C25D 3/30; C22B 9/02; H01L 21/302

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: tin, Sn, deposit, alpha, particle, emission, refine

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2009-0098012 A1 (YUICHIRO SHINDO et al.) 16 April 2009 See paragraphs [0042]-[0054] and claims 3, 6.	1-10
Y	US 2011-0089567 A1 (HISAO ISHIKAWA et al.) 21 April 2011 See paragraph [0064], claim 11 and figure 1.	1-10
A	US 6685820 B2 (KUO-CHIN CHEN et al.) 03 February 2004 See column 2, line 24 - column 3, line 50, claim 1 and figure 1.	1-10
A	JP 2010-024517 A (TOPY IND. LTD. et al.) 04 February 2010 See paragraphs [0022]-[0032], claim 1 and figure 1.	1-10
A	KR 10-0816666 B1 (ROHM AND HAAS ELECTRONIC MATERIALS, L.L.C.) 27 March 2008 See paragraphs [0010]-[0052], claim 1 and figure 1.	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search

27 September 2013 (27.09.2013)

Date of mailing of the international search report

27 September 2013 (27.09.2013)

Name and mailing address of the ISA/KR

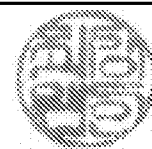
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/046064

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