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RECOVERY OF WASTE SEMICONDUCTORS FOR CVD PRECURSORS

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Abstract

The newly patented method for regeneration of ultrapure silicon and germanium via magnesium silicide and magnesium germanide from waste photovoltaic (PV) cells, broken germanium lenses and waste magnesium chips was utilized to obtain chemical vapour deposition (CVD) precursors for application in electronics, optics or nanoparticles synthesis. Magnesium silicide and germanide were prepared directly by thermal synthesis from waste materials in optimized tube reactor at 400°C and 5 Pa. X-Ray Diffraction (XRD) confirmed 97.9% respective 95% purity of products. The presence of silicon and germanium hydrides (CVD precursors) prepared by acid hydrolysis in the second step of the process was verified by Gas Chromatography–Mass Spectroscopy (GC/MS) and Fourier Transform Infrared Spectroscopy (FTIR). The crude, unrefined mixture of silicon hydrides served as raw material for CVD experiment at different substrates. SEM images confirmed occurrence of various micro and nano particles which could be used in electronics, optics and catalysis.

Introduction

Photovoltaic panels are currently commonly used as a source of renewable energy. They contain except for silicon many other elements. Germanium has also become an important material for today's highest efficiency solar cells¹, too. The effort of many countries to improve the state of the air, and contributory policy on renewable energy sources caused that the number of installed PV panels per year has been rapidly growing. However, the first generations of silicon PV panels have come to the end nowadays². Moreover, silicon together with germanium are also commonly used in the field of semiconductors, transistors, electronics and optical devices³. Nevertheless, the new use of germanium in high technological industrial applications, which has caused the scarcity of germanium resources, increased its price up to 2000 USD/kg in 2015. Therefore, it has been attractive to process raw materials and electronic scrap even of very low germanium content. This fact initiated significant efforts to improve the efficiency of germanium recovery, similarly as recycling from waste products⁴. However, the reuse of silicon and germanium for electronics and PV purpose requires their top purity and established recycling and purification methods highly economically and ecologically demanding⁵. One of these methods is based on thermal treatment with subsequent series of chemical leaching, extraction and separation of desired elements. Crushing and milling, series of separations and extraction or electrolysis is another used method for silicon and germanium recycling from PV waste^{6–9}. Mentioned methods often produce silicon and germanium in purity which is insufficient for their reuse in electronics and photovoltaic devices. Therefore, the next purification steps are required^{4,9}. Refining of silicon and also germanium is based on their conversion to volatile compounds mainly chlorides and chlorhydrides by the reaction with hydrogen chloride or chlorine at higher temperature. Prepared silicon chlorides and hydrochlorides need to be separated by repeated distillation and then could be reduced by hydrogen and thermally decomposed by Siemens process at 1100°C. In the case of germanium, separated chlorides are hydrolysed to germanium oxide and then two-step reduced by hydrogen at 700°C to produce ultrapure germanium^{10–12}.

The chemical vapour deposition (CVD) is a method employed to create silicon and germanium layers in semiconductor, electronics and optical industry and is also used for nanoobjects synthesis¹³. As a silicon and germanium precursors, silicon hydrides (silanes) and germanium hydrides (germanes) have been usually used. Their synthesis, especially higher hydrides even germysilanes, is very complicated which is significantly reflected in their price and lack of availability¹⁴. Varma and Cox¹⁵ prepared germysilanes ($\text{Si}_x\text{Ge}_y\text{H}_z$) from chloregermane and silyl potassium in 20 per cent yield. It can also be prepared by the interaction of germyl sodium with bromosilane in 7.8 percent yield¹⁶. Silane (SiH_4), may be efficiently prepared by the reaction of silicon tetrachloride with lithium hydroaluminate¹⁷, and germane (GeH_4) may be efficiently prepared by the reaction of aqueous germinate (IV) with aqueous hydroborate¹⁸. However, none of the methods preparing silanes or germanes from aqueous or non-aqueous solutions gives decent yields of the higher hydrides with the general formula $\text{Si}_n\text{H}_{2n+2}$ and $\text{Ge}_n\text{H}_{2n+2}$. The higher silanes¹⁹ and germanes²⁰ may be prepared in good yields by passing silane and germane, respectively, through an ozonizer-type silent electric discharge²¹ in good yields, regrettably, in high costs. For that reasons, the newly patented low-cost technology for ultrapure silicon, germanium and their CVD precursors via magnesium silicide and magnesium germanide from waste materials is presented.

Experiment

The end of life PV cells as a source of silicon with purity over 90 %, broken infrared lenses as a source of germanium with purity over 99 % and waste magnesium chips with purity over 90 % were used as a raw materials for preparation of magnesium silicide and magnesium germanide. For preparation of magnesium silicide the PV cells were milled and mixed with magnesium chips in molar ratio $\text{Mg} : \text{Si} = 2.1 : 1$. For preparation of magnesium germanide, magnesium chips were mixed with milled lenses in molar ratio $\text{Mg} : \text{Ge} = 2.1 : 1$. The particle size of the reaction mixture was smaller than $200 \mu\text{m}$ in both cases. Prepared mixtures were homogenized and filled into the closed tube reactor with 1 mm small vent-hole, evacuated to 5 Pa, preheated to 120°C and then heated to final temperature 400°C with temperature rate of $15^\circ\text{C}/\text{min}$. The end of the reaction was detected by pressure changes and did not exceed 25 minutes. Prepared samples were characterized by XRD, Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Spectroscopy (EDX) and Raman spectroscopy and hydrolysed by 25% phosphoric acid solution at 5 Pa to produce corresponding hydrides, which were analysed by FTIR and GC-MS.

Discussion and results

The economic aspects of regeneration and purification of silicon and germanium from waste together with complex preparation of their hydrides are challenging task. This work follows up on our previous publication⁹, in which reactor, reaction conditions and time for preparation of magnesium silicide were thoroughly studied and optimized. The other publication⁴ then confirmed, that the optimized arrangement is also proper for preparation of magnesium germanide. In this reaction the 5% molar excess of magnesium was used to compensate its evaporation during reaction, because the reaction conditions allows to change the phase equilibrium of magnesium even it can sublime. The small diameter of reactor's vent-hole was designed to prevent massive evaporation of magnesium and simultaneously enabled evacuation of air humidity and other impurities from the reaction mixture and reactor. Based on this findings the real application of hydrides prepared from magnesium silicide was also investigated. Preparation of magnesium silicide and also germanide is exothermic reaction described by Equations 1-3.

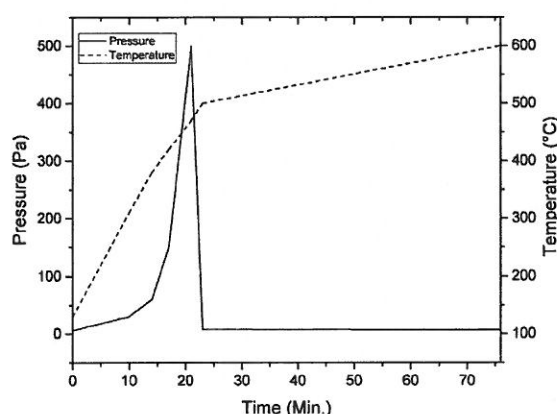
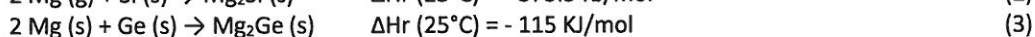
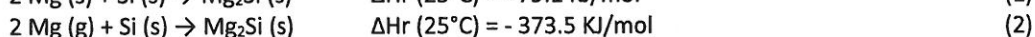
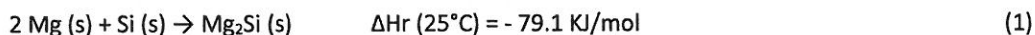


Figure 1. Pressure dependence on time at rising temperature during magnesium silicide preparation

The Figure 1 depicts pressure changes during magnesium silicide preparation at rising temperature with rate $15^\circ\text{C}/\text{min}$ until 500°C and then with $2^\circ\text{C}/\text{min}$ until final temperature 600°C . The experiment was realized to find minimal reaction temperature and to observe pressure changes, which confirmed sublimation of magnesium by rapid increase of pressure at 400°C . The end of the reaction was characterized by rapid pressure decrease, which signified depletion of magnesium vapour by passed reaction. The reaction time did not exceed 25 minutes after the start of heating. It is also evident that the direction of temperature line changed at about 400°C most probably by energy consumption for magnesium sublimation. The pressure dependence was practically identical to magnesium germanide preparation. The composition of prepared products is summarized in Table I.

Table I

Composition of prepared samples at 400°C after 25 minutes from XRD

Products [w %]	Mg ₂ Si	Mg ₂ Ge	Mg	Si	Ge	Undefined
Samples [mol]						
2.1Mg : 1Si	97.9	-	2.0	0.1	-	0.0
2.1Mg : 1Ge	-	95.0	3.0	-	-	2.0

The results in Table I show, that the conversion of silicon to desired product was over 97 % and the conversion of germanium was total. The XRD characterization together with Raman spectroscopy confirmed good crystallinity of prepared samples and SEM/EDX verified fine homogeneity see Figure 2.

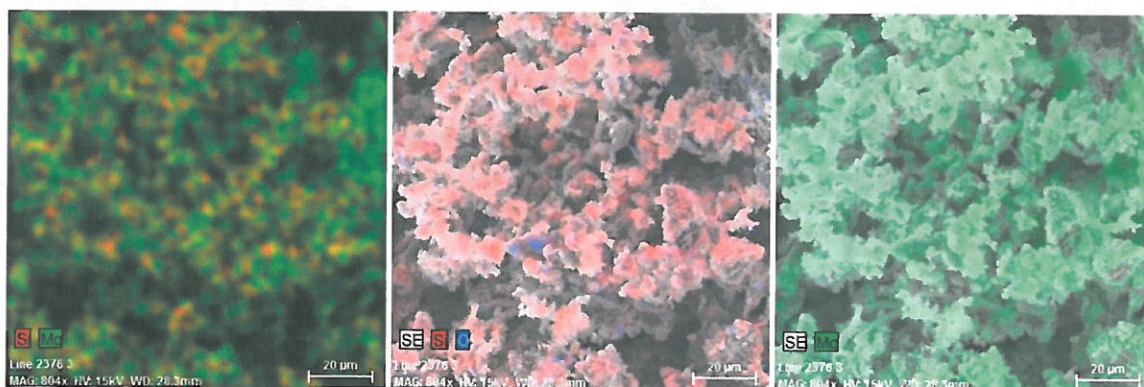
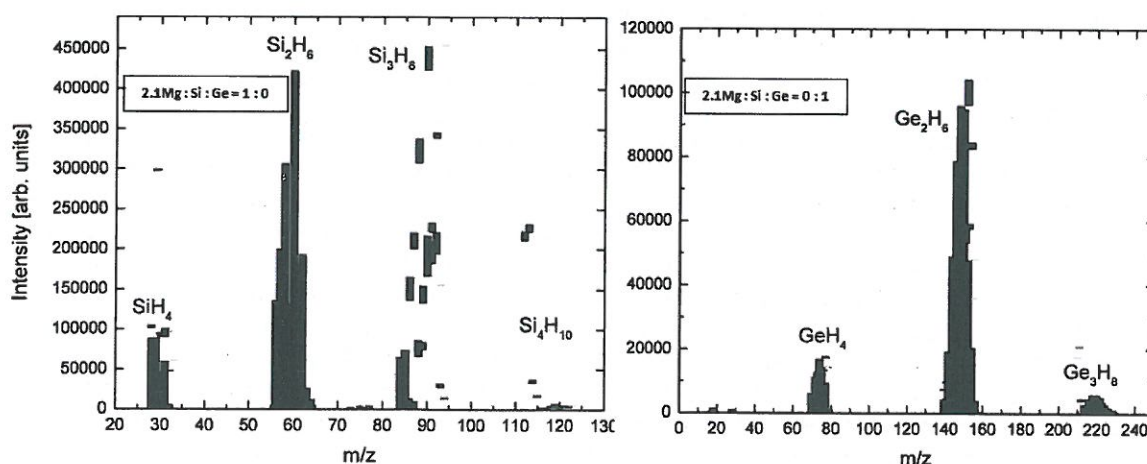
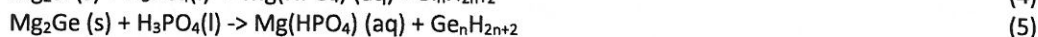


Figure 2. SEM/EDX pictures of prepared magnesium silicide. Element mapping: Silicon (red), Magnesium (green)

Mentioned requirements meet the conditions for successful hydrolysis experiment, which is described by Equations 4 and 5. Prepared hydrolysis products were characterized by GC/MS and FTIR as seen on Figure 3.

Figure 3. GC/MS analysis of individual hydrolysis products of samples from table I by 25% H₃PO₄

The results demonstrated by Figure 3 confirmed presence of desired hydrides, silanes, in the case of magnesium silicide hydrolysis and germanes, in the case of magnesium germanide hydrolysis. The only by-product of hydrolysis was magnesium hydrogen phosphate trihydrate solution and minimal silicon or germanium residues. The characterization of the by-product confirmed high conversion of hydrolysed silicide and germanide to silanes and germanes. Separation of individual hydrides from mixture was also successfully verified in our previous manuscript⁴ easily by distillation based on big difference in boiling points.

Nevertheless, the crude gaseous product of magnesium silicide or germanide hydrolysis could be directly used as a precursor for CVD deposition. Thus, the crude gaseous product of magnesium silicide was collected into cuvette and decomposed at 400°C on three various substrates; copper, nickel and stainless steel. The substrates were observed by SEM and obtained results are summarized in Figure 4.

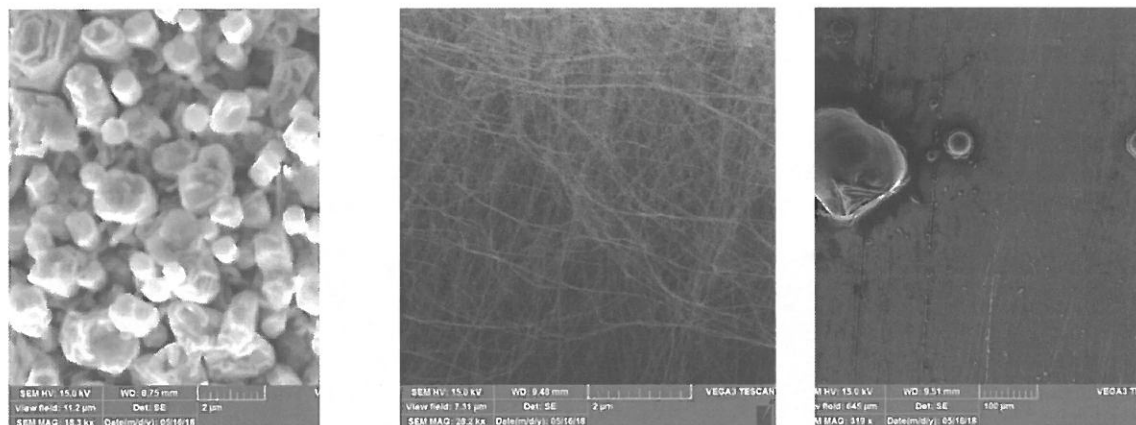


Figure 4. SEM pictures of particles created by CVD of silicon hydrides mixture at 400°C on (from left) copper, nickel and stainless steel substrates

As seen on SEM images, unrefined and unseparated mixture of prepared silanes was decomposed on various substrates and produced different structures. The copper substrate was covered by microcrystals, based on the literature and morphology, its probably $\text{Cu}_3\text{Si}^{13}$. The middle image depicts nanowires prepared on nickel substrate which correspond to Ni_3Si_2 nanowires prepared by CVD on nickel substrate in literature²². The last image shows drops growing from substrate, which could be some kind of iron silicide. All the created structures will be studied in details and subsequent application for electronics, photovoltaic and catalysis will be thoroughly investigated.

Conclusion

Established technologies for regeneration of silicon and germanium from PV panels and electronics have been highly economically, ecologically and technologically demanding with series of steps and relatively low efficiency. Moreover for their reusing in electronics and photovoltaics subsequent purification steps are required. However, production of electronics, PV components and also related waste has been still rising. From that reasons, newly patented low cost technology for silicon and germanium reuse from waste was investigated. It was confirmed, that the end-of-life PV cells, broken germanium lenses and waste magnesium chips could be successfully used as a raw materials for magnesium silicide and magnesium germanide prepared by direct thermal synthesis at 400°C under 5 Pa after 25 minutes. The conversion of silicon to magnesium silicide was almost 98 %, in the case of magnesium germanide 95 % which was confirmed by XRD. Prepared magnesium silicide and magnesium germanide were then hydrolysed by 25% phosphoric acid solution to produce silicon and germanium hydrides, which are commonly used as CVD precursor for deposition of ultrapure silicon and germanium in electronics, optics and could be also used for nanostructures synthesis. The composition of produced hydrides were characterized by GC/MS and FTIR, which confirmed presence of silane, disilane, trisilane, tetrasilane as a product of magnesium silicide hydrolysis and germane, digermane and trigermane as a product of magnesium germanide hydrolysis. Finally, the crude, unrefined mixture of silicon hydrides was successfully decomposed as CVD precursor at 400°C on the surface of copper, nickel and stainless steel substrate. SEM pictures of their surface after reaction showed that various types of micro and nanostructures were prepared. Created particles could find employment in electronics, photovoltaics and catalysis.

Acknowledgement

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