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ScienceDirect
Journal of Taibah University for Science 10 (2016) 221–226
Journal of Taibah University for Science
www.elsevier.com/locate/jtusci

Analysis of the natural activities of radionuclides, heavy metals, and other poisonous elements in lead-free Sn–6.5Zn solders with different alloying elements

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Available online 17 June 2015

Abstract

Problem statement: Sn–Zn solders are candidate alternatives to Sn–Pb-based solder alloys. With the increasing requirement for lead-free solders, the reliability of successor solders in microelectronics assemblies is in high demand. The elimination of radionuclides, heavy metals, and other poisonous elements in lead-free Sn–6.5Zn solders in the microelectronics industry is a worldwide goal. As a result, it is useful to identify the natural concentrations of radioactive nuclides, heavy metals and other poisonous trace elements (both macro- and micro-element contents), such as Au-196, Th-227, Ag-110M, Fe-59, Zn-65, Rb-89, Rh-106M, Bi-207, Cs-137, Eu-154, Sb-126, Eu-152, Co-56, Co-58, Co-60 and K-40. If this lead-free solder contains high concentrations of natural radioactive nuclides, then workers handling it might be exposed to significant levels of radiation. Therefore, it is important to determine the levels of radioactive nuclides in this solder to protect workers; these levels provide background for the safety rules and precautions that should be applied for those working in this field.
Approach: The levels of natural radionuclides (^{238}U, ^{232}Th, and ^{40}K) and their daughter products contained in Sn–6.5Zn solders have been estimated via gamma-ray spectrometry using a 100% Hyper-Pure Germanium (HPGe) detector.
Results: The mean activities due to radionuclides, heavy metals, and other poisonous elements were measured, and the results are summarised in tables.
Conclusion: The results of this assessment obtained by gamma-ray spectroscopic analysis indicated the presence of high levels of natural radioactivity, heavy metals and other poisonous elements. This result implies that a comprehensive study should be conducted to protect workers from high doses of hazardous substances.

Keywords: Natural radionuclides; Equivalent activity; Annual effective dose; Radiation hazard index; Gamma spectrometer; NAA; Poisonous elements

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Peer review under responsibility of Taibah University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jtusci.2015.05.002

1. Introduction

Due to world-wide environmental concerns regarding Pb toxicity, the electronics industry is moving towards the adoption of lead-free solders as substitutes for lead-bearing solders [1,2]. Many promising Sn-rich alloys have been recommended to replace traditional Sn–Pb solders. These lead-free solders commonly have low elastic moduli to accommodate CTE mismatches between the die and substrate, good electrical conductivity, high surface tension in the liquid state to align the parts during assembly, and can be placed via several different techniques. Unfortunately, the incorrect common belief is that lead-free solders have no natural radioactive nuclides, heavy metals, or other poisonous trace elements because they do not contain lead that is, because the lead-free solder is Sn based and Pb is a natural trace impurity in Sn, lead-free solders should not contain any hazardous impurities. However, among these solders, the Sn–Zn system has been considered to be one of the most promising candidates for Pb-free solders due to its lower material cost and low melting point (198 °C), which is close to that of Sn–Pb (183 °C) [3]. Nevertheless, several problems must be addressed to increase the practical application of Sn–Zn solders in electronic manufacturing, such as the poor wettability, easy oxidation and some reliability issues [4,5]. Unfortunately, solders also contain low levels of radioactive isotopes that emit various forms of gamma-ray radiation. Because the solders in a wafer bump are very close to the active area of the chip, the gamma-ray radiation can deposit enough energy in a memory cell on the chip to erase the stored information; in addition, the radiation can affect the workers in this field because human beings are always exposed to natural radiations from their surroundings. An established fact is that over 60 radionuclides can be found in the natural environment. Natural radioactivity is common in the rocks and soil that comprise our planet, in water and oceans, and in our building materials and homes [6]. Therefore, the assessment of the gamma radiation dose from natural sources is of particular importance as natural radiation is the largest contributor to the external dose of the world population [7,8]. This natural exposure implies that a comprehensive study should be conducted to determine the reasons for the high levels of radionuclei, heavy metals and other poisonous elements in the lead free solder alloy samples.

One common approach to improve the properties and reliability of lead-free solders is to identify and eliminate the radionuclides, heavy metals, and other poisonous elements in lead-free solders in the microelectronics industry. Therefore, the goals of this work re to identify and determine the concentration of natural radioactivity due to uranium, thorium, potassium, heavy metals, and other poisonous elements in Sn–6.5Zn lead-free solders doped with different alloying elements and to measure the surface radiation dose rate, the radium equivalent activity and the radiation hazard index (Table 1). The absorption of these elements, including toxic ones, is higher in infants than older children and adults [6]. These toxic substances have a severe and rapid impact on the central nervous system of newly born children. Finally, the determination of the elements present in tin ore samples is performed using the XRF-technique.

Table 1
The natural radionuclides, their gamma lines used and their intensities.

Parent nuclide	Daughter nuclide	γ-Ray energy (keV)	Abundance (%)
226Ra	214Bi	1120.28	14.9
	214Bi	1764.52	16.07
232Th	228Ac	911.16	29.0
	208Tl	2614.7	36.0
40 K	–	1460	10.67

2. Materials and methods

Commercially pure elements of Sn, Zn, Bi and Cu were used to produce the solder alloys in this study. The composition of the solder alloys considered in this study were Sn–6.5Zn, Sn–6.5Zn–1.5 wt.% Cu and Sn–6.5Zn–3.0 wt.% Bi alloys. The process of melting was performed in a vacuum arc furnace under the protection of a high purity argon atmosphere at 800 °C for approximately 1 h. To obtain a homogeneous composition within the ingots, the alloy samples were remelted three times to produce rod-like specimens with a diameter of approximately 1.5 cm. The solder alloys were mounted into clean containers and then measured for 10,480 s. The energy and intensity of the various gamma-ray lines were measured using a system based on a Canberra coaxial High-Purity Germanium detector (HPGe) Fig. 1 with a relative efficiency of 100%. The energy resolution was 2.1 keV full-width at half

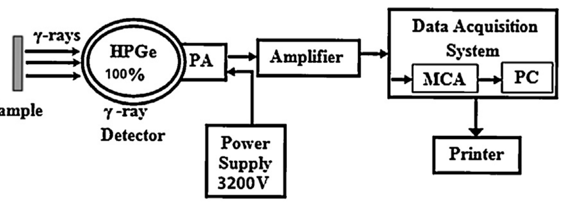

Fig. 1. Blocked diagram of HPGe γ-ray spectrometer system.