



Risk of transition to lead-free in the space sector: Sn whisker growth in thermal vacuum conditions from submicron Sn layer

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ARTICLE INFO

Keywords:

Sn whisker
High vacuum
Space environment
PVD
Reliability
TEM

ABSTRACT

Sn whisker growth was investigated from submicron Sn layers on Cu substrates in thermal vacuum conditions to compare the growth differences in ambient and space conditions. Cu substrates were covered with 500 nm thick Sn by PVD. The samples were kept at 50 °C and 8.3×10^{-6} mbar for 1000 h in order to simulate the space conditions. Numerous Sn whiskers were found on the samples after some days of sample preparation. More but shorter whiskers with different structures were developed in a vacuum than in ambient conditions before. The vacuum-grown whiskers had segmented block-like bodies with a plain surface, while ambient-grown whiskers had a twisted body with grooves. TEM investigations found a weak correlation between the crystal structure and the shape of the different whiskers. However, it proved that the high mechanical stress of the Cu_6Sn_5 intermetallic layer growth initiated the interface flow mechanism, which transported Cu_6Sn_5 into the whiskers. The vacuum-grown whiskers contained approximately half the amount of Cu_6Sn_5 inclusions than the ambient-grown ones, which could be related to the more uniform stress relaxation of the oxide-free surface in the vacuum. The higher amount Cu_6Sn_5 inclusions could cause the twisting of the whisker bodies in ambient conditions.

1. Introduction

The lead-free change in the soldering technology greatly impacted the microelectronics industry in the early 2000 s. Totally new material systems (solder alloys, surface coatings, fluxes) went into production in 2006. The space sector was out of the scope of the RoHS Directive, although they dealt with the surrounding situation. The European Space Agency (ESA) published guidelines for creating a lead-free control plan in 2012 to evaluate the lead-free risks on space electronics [1]. In 2020, ESA published the roadmap for lead-free transition [2]. The space sector is still not forced by the law to change lead-free, but they identified the risks of not doing so, which come from two sources: regulatory and market pressures. From the regulatory side, a new front has opened with the REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) directives. Lead (Pb) is already included in the REACH candidate list, so there is a risk for the space sector that, in the future, the application of Pb will be requested for authorization [2].

The space sector is also suffering from increasing market pressures.

Due to the overall transition to lead-free, the space industry cannot avoid using components and printed circuit boards (PCBs) with lead-free coatings and surface finishings. Furthermore, regulatory pressure may also cause a difficult market availability for leaded solder alloys [2]. ESA published an authorization plan for lead-free change, which contains the earliest date to 2026 [3]. At the moment, ESA is putting great effort into researching the risk of the lead-free transition for electronics used in the space environment. Fig. 1a shows the main targets [3]. According to the ESA roadmap (Fig. 1a), one of the main identified risks of lead-free transition in the space sector is Sn whisker growth.

Sn whiskers are dangerous surface defects that grow due to mechanical stress acting on high Sn-content objects. They cause reliability risk via short circuit formation since they can conduct electricity, and their length can reach hundreds of micrometers, which is in one range with fine-pitch electronic components used recently. According to the shape, three main whisker types are distinguished: filament (the most dangerous), nodule, and hillock (Fig. 1b). The filaments and hillocks are usually monocrystalline, and the nodules have polycrystalline structures

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<https://doi.org/10.1016/j.matdes.2025.113637>

Received 6 December 2024; Received in revised form 13 January 2025; Accepted 15 January 2025

Available online 16 January 2025

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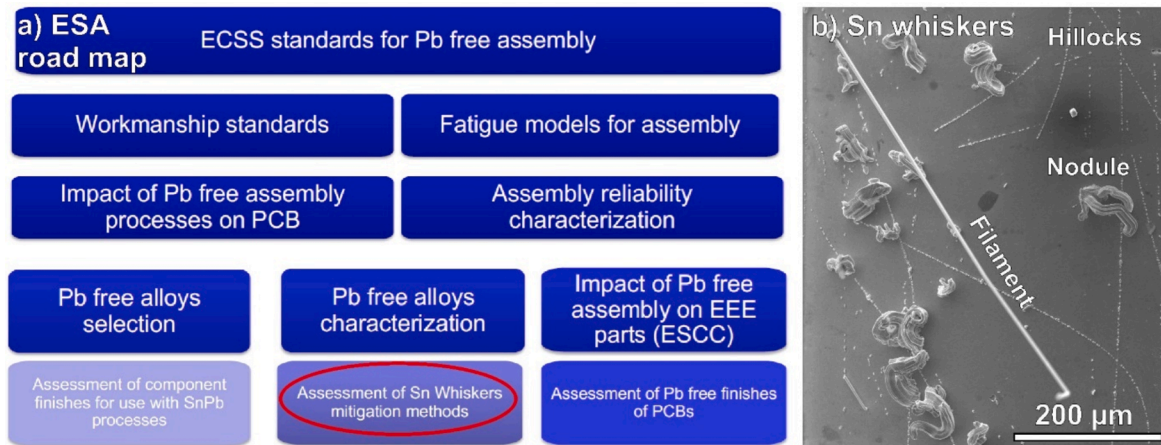


Fig. 1. A) esa road map targets[3]; b) whiskers on Sn surface finishing of a component lead (from a previous research of B.I.).

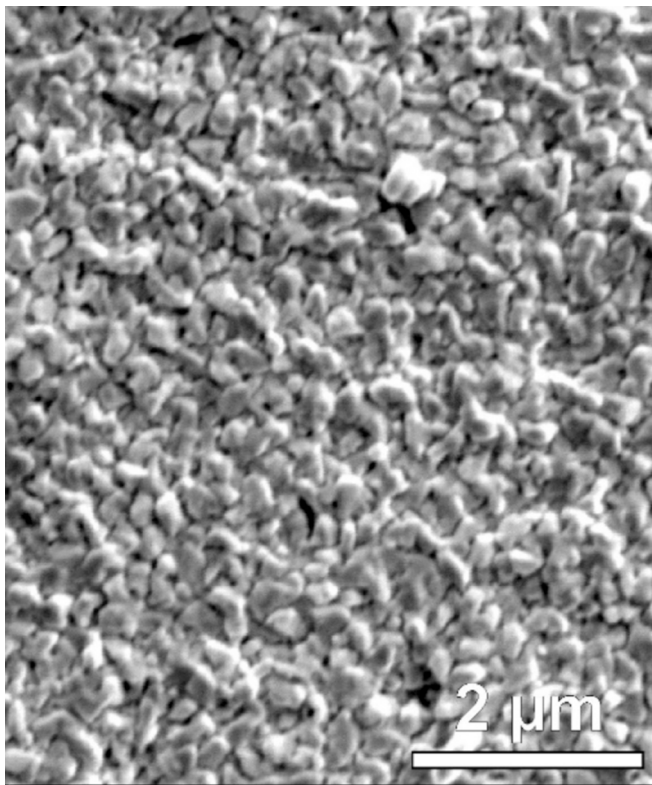


Fig. 2. SEM micrograph of the evaporated Sn layer showing the surface topography.

[4]. Sn whiskers can grow on the surface of any pure or high Sn-content objects, like solder joints, component leads, and solder pad finishes. Sn whisker growth is always induced by mechanical stress acting on the surface of the Sn object. This stress can originate from a direct mechanical load, residual stress in the Sn layer during the deposition process, volumetric expansion during material transformations like oxidation of Sn or intermetallic layer growth at the interface of Sn and the substrate, and thermomechanical effects of different coefficients of thermal expansion in the system [5]. Finally, the Sn whisker growth is the stress relaxation answer of the Sn layer on the mechanical.

The research about Sn whisker growth in a vacuum or inert atmosphere started many decades ago. However, it is much less wide than the research in ambient conditions. Arnold mentioned in 1959 that whiskers can also grow in evacuated or inert gas atmospheres. The example was

an evacuated glass-enclosed quartz crystal resonator where tin whiskers were found on the tin-plated support wires [6,7]. Richardson and Lasley [8] reported that Sn whisker caused problems in spacecraft electronics due to vacuum metal arcing, as did Westerhuyzen et al. [9]. Not only was Sn concerned about the issue, but Ag as well. Umalas et al. [10] demonstrated electron beam-induced rapid growth (during SEM analysis) of silver nanowhiskers from silver nanowire networks coated with TiO_2 by the sol-gel method.

Brusse et al. [11,12] emphasized that Sn whiskers grown in a vacuum pose a very serious reliability risk to electronic circuits, much more serious than that occurs in atmospheric conditions. The general risks fall into three categories: i) whiskers can break loose and bridge component leads or interfere with optical surfaces; ii) in low voltage and high impedance circuits, there can be insufficient current available to fuse the whisker open and a stable short circuit results; iii) in vacuum, if the current is above few amperes, and the supply voltage is above 18 V, the whisker can fuse open and the vaporized Sn can initiate a plasma that can conduct more than 200 amps [13]. Tin whisker-related failures caused several GIDEP Alerts and Problem Advisories: complete loss of satellite operations, a tin whisker short (metal vapour arc in vacuum) from pure tin plated relay was experienced (Galaxy IV, Galaxy VII, Solidaridad I) [11].

Williams et al. [14] studied the mechanisms of Sn hillock growth induced by in-situ indentations in SEM in a vacuum (1.3×10^{-4} Pa). Considerable mass flow between indentation places was detected, with some indentation places exhibiting extensive (linear or parabolic) growth, while the growth of others was stopped within 100 h. They could postulate when stress was relieved slowly, and hillock grew nearly linearly over time. When stress was relieved quickly, a sigmoidal-type curve (arresting growth) occurred. Moon et al. [15] cleaned a part of a bright Sn-Cu electrodeposited film from the oxide using an Ar^+ ion beam and aged it for 9 days in the 2×10^{-9} Pa Auger system chamber. The results suggested that Sn whiskers can grow regardless of the presence or absence of surface oxides; however, longer whiskers were found on the oxidized parts of the samples. Barsoum et al. [16] found that the Sn surface exposed to air performed significantly more whiskers than the Sn surface held in a vacuum; furthermore, the whiskers formed in the air were significantly longer. They investigated several materials, In, Al, Sn, etc.

Suganuma et al. [17] investigated the Sn whisker growth from pure Sn plating on ceramic substrates during thermal cycling (-40 to 125°C) both in air and in vacuum (10^{-4} Pa) conditions. The CTE difference between Sn plating and the Al_2O_3 substrate was large enough to create Sn whiskers. They observed that Sn whisker growth in a vacuum was more intensive than in air. Thinner and longer whiskers grew in a vacuum than in air, while the whisker density was not influenced by the atmosphere. Jo et al. [18] have made a comparison between thermal stress-

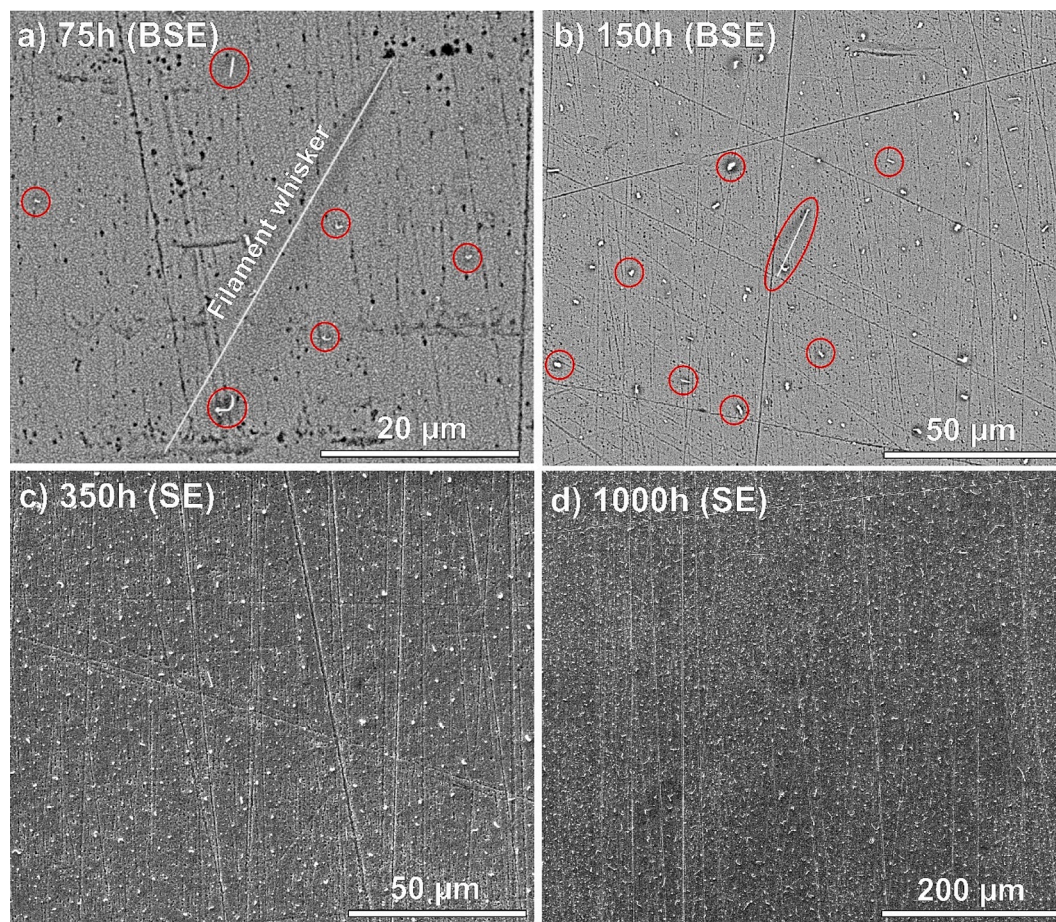


Fig. 3. SEM micrographs of the samples during the thermo-vacuum test: a) 75 h (BSE); b) 150 h (BSE); c) 350 h (SE); d) 1000 h (SE).

driven (-20 to 80 °C) Sn whisker growth from matte Sn electroplating on Alloy42 in air and in vacuum (10^{-4} Pa). They experienced that Sn whiskers grew thinner and faster in vacuum than in air due to the thermal stress distributions in the electroplatings. In the case of ambient conditions, they found oxidized grain boundary cracks, which determine the stress concentration that causes the whisker growth. Oxidation could not cause cracking in a vacuum, hence causing thin and straight whiskers. Ichimaru et al. [19] investigated Sn whisker growth from pure Sn platings on Ni/Cu and Alloy42 substrates by different thermal cyclings in air and vacuum. They also found longer and thinner whiskers in vacuum than in air, but there was no correlation between the density of the whiskers and the storage condition.

In further related studies, Oudat et al. [20] could develop whiskers from Sn thin film on a glass substrate in a vacuum by x-ray and gamma-ray irradiation, thus demonstrating the electrostatic nature of the whisker development. Wang et al. [21] studied the whisker growth from patterned Sn thin films on Si substrate and found that the area of the Sn thin film effect of whisker development. They observed characteristically higher whisker densities as the patterned Sn area size increased, thus demonstrating the role of lateral Sn diffusion in the film on whisker growth. Liu et al. [22] observed rapid whisker growth on Ti_2SnC -Sn in constant vacuum and ambient conditions as well. Furthermore, Zhang et al. [23] showed the role of active Sn atoms in whisker growth from mechanochemically decomposed Ti_2SnC . The released Sn atoms have a high chemical potential, which drives them to the Sn whiskers' roots, enhancing the whisker growth. Tand et al. [24] got similar results in the case of oxygen-mediated decomposition of the same Ti_2SnC . Wang and Wang [25] reported that in extreme environments such as space, multiple factors build the environments, including vacuum, magnetic and electric field, magnetic storm, weightlessness, radiation, etc., which

might result in a complex and varied mechanism of Sn whisker growth.

Consequently, Sn whisker growth is an existing issue in space conditions, and only a few results were obtained in thermal vacuum conditions. The whisker-caused risk can grow with the change to lead-free in the space industry. In our work, we investigated Sn whisker growth from submicron Sn films in thermal vacuum conditions to compare the growth differences between ambient and space conditions.

2. Materials & methods

Pure Cu substrates with a 9 cm^2 area were used for the study. Before the coating procedures, the Cu substrates were heat-annealed at 150 °C for 2 h to release the residual stresses caused by sheet rolling and cutting processes. After that, the Cu substrates were chemically degreased using a Uniclean 251 solution (Atotech) for 5 min at 48 °C, and etched in 10% H_2SO_4 solution for 1 min to remove the superficial layer of copper oxides. The relaxed and cleaned Cu substrates were covered with pure pure (99.99 %) Sn by physical vapour deposition (PVD) method in a Balzers BA 510 evaporator. First, the surface of the samples was neutralized by ion bombardment in the evaporator. The resistive evaporation technique was applied with a Wolfram or Molybdenum boat, which was filled with Sn and heated up with high voltage and current (2.5 kV and 9 A) in a vacuum (10^{-4} Pa). The evaporation time was 10 s. The SEM micrograph in Fig. 2 shows the evaporated Sn layer where the Sn grains are also well visible. The PVD process resulted in an Sn mono-layer, so the Sn grain size observed on the surface correlates well with the layer thickness. The thickness of the Sn layer was measured by an Alpha-Step 500 surface profiler, and it was approved to be between 400 and 500 nm.

The samples were kept at 50 °C constant temperature and 8.3×10^{-6} mbar vacuum for 1000 h. The surface of the samples was monitored after

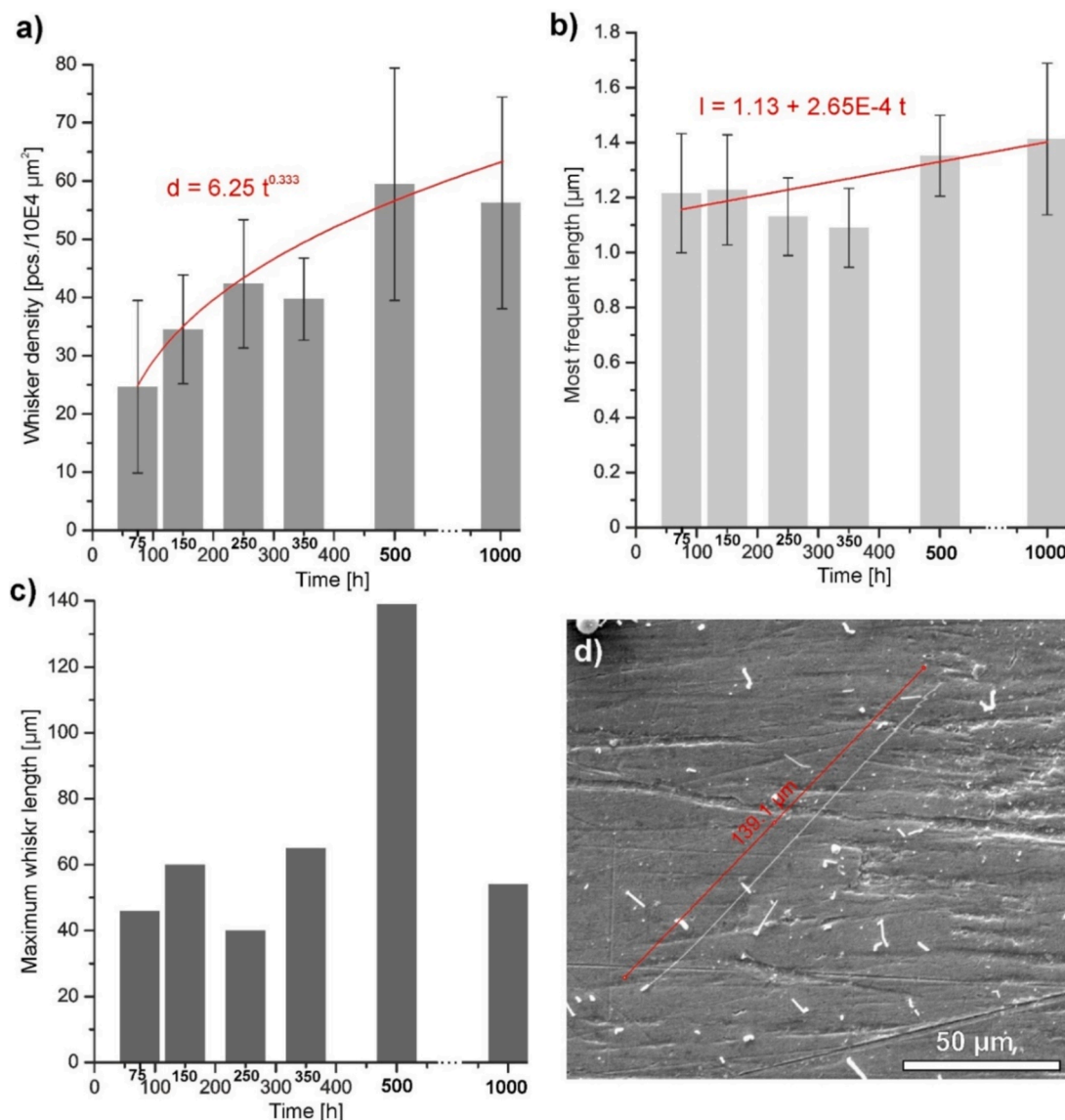


Fig. 4. Sn whisker statistics: a) whisker densities; b) most frequent length; c) maximum length; d) longest detected whisker during the study.

75, 150, 250, 350, 500, and 1000 h by a FEI Inspect S50 scanning electron microscope (SEM). The aim of the frequent checking was to investigate the dynamics of the whisker growth in time since, according to our previous experiments, harsh whiskering was expected on samples at the beginning of the test [26]. At the end of the test, the morphology of the whiskers was observed by a Thermo Scientific Quattro SEM with a field emission gun. The test was always a „non-return” type, which meant that the investigated samples were not returned to the vacuum chamber after the SEM investigation to avoid the effect of the oxidation (so at each checkpoint, different samples were investigated). N₂ flushing was applied during the sample removal from the chamber in order to avoid the oxidation of the samples, which stayed further in the test. This procedure needed to be used due to the relatively fast oxidation of the Sn in the ambient atmosphere.

A code in Matlab LiveScript was developed for semi-automatic analyses of the whisker statistic due to the large number of whiskers. The code is based on the following main steps: i) loading the image; ii) determining the scale factor for length conversion (px to μm); iii) interactive thresholding; iv) noise filtering by 3px median filter; v) noise filtering by eliminating features shorter than ~ 1 μm; iv) morphological close and measuring. The measured properties included:

- The density of whiskers (pieces/μm²).
- The most frequent length (ellipses were fitted on the whiskers, and the major axis length was calculated). The most frequent length is a better measure than the average length since it gives length information about the majority of the developed whiskers without the outlier values.
- The maximum length (rectangles were fitted on the features, and the diagonal length was calculated). In the case of the long whiskers, the rectangle fitting has a lower error than the ellipses.

It has to be noted that the SEM image is only a planar mapping and cannot fully reflect the spatiality of the whisker. Thus, the lengths of the whiskers in the SEM images might not be the real length of the different whiskers.

Cross-sections and lamellae were prepared from the Sn whiskers for transmission electron microscopy (TEM) by a Thermo Scientific Scios 2 – focused Ga⁺ ion beam (FIB) sputtering. Before ion milling, the surface of the samples was covered with a platinum layer to protect the top surface from damage by the high-energy gallium ion beam, and they were transferred on a Cu support grid. The lamellae were observed using a Thermofisher THEMIS 200 aberration-corrected TEM/STEM.

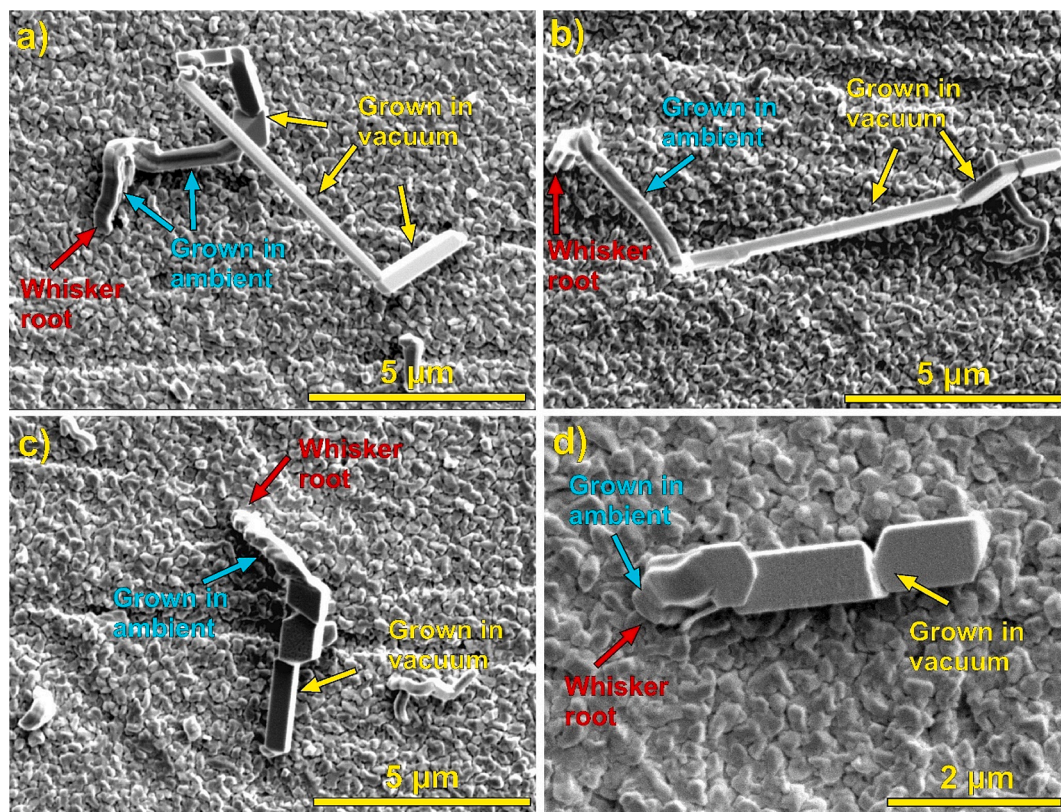


Fig. 5. SE SEM micrographs of Sn whisker morphologies in vacuum and ambient atmosphere: a) whisker #1; b) whisker #2; c) whisker #3; d) whisker #4.

Spectrum imaging using scanning TEM (STEM) and energy dispersive x-ray spectroscopy (EDS) analysis was used to map the elemental composition and distribution (EDS map) of the samples. The crystallographic structure of the Sn whiskers was determined by Fast Fourier Transformation (FFT) and the selected area electron diffraction (SAED) technique.

3. Results

The first whiskers were detected already after 75 h of thermo-vacuum testing. Fig. 3a presents an approximately 60 μm long filament whisker (and some shorter ones) only after 75 h of the deposition of the Sn layer. All lighter eruptions in the SEM micrographs were whiskers; some of them were marked by red circles for easier identification in Fig. 3a and b. The number and the length of Sn whiskers considerably increased over time. The number increase is clearly visible in Fig. 3b and c (represents 150 and 350 h), which have the same magnification. At the end of the thermo-vacuum test, the entire surface of the samples was covered with high-density Sn whiskers (Fig. 3d). It is worth comparing the contrast differences between the BSE and SE SEM micrographs in Fig. 3. From the point of counting the whiskers, the SE micrographs are more beneficial, but for the morphological evaluation of the whiskers, the BSE micrographs are more valuable.

The Sn whisker growth was statistically evaluated (Fig. 4). As was visible in Fig. 3a, numerous whiskers had already grown during the first days of the test; their density exceeded 20 pcs./ $10\text{E}4\ \mu\text{m}^2$ (Fig. 4a). After 500 h, the whisker density reached 60 pcs./ $10\text{E}4\ \mu\text{m}^2$, which crowd is well represented in Fig. 3c and d. The most frequent length was relatively small during the whole test, between 1.2 and 1.4 μm (Fig. 4b), which means that plenty of short whiskers grew. Fig. 4c shows the longest detected Sn whiskers at each observation step of the test. They were typically between 40 and 60 μm . The absolute longest detected whisker was 139.1 μm at 500 h (Fig. 4d). Whiskers over 50 μm could be dangerous for fine-pitch microelectronics. The nature of Fig. 4b and c

indicate that the whiskers reached their maximum length very fast (in some days) after they started to grow. Similar results were reported in [27]. The increase of the whisker statistics with the time was not totally monotonous since the test was a non-return type (the investigated samples were not returned to the vacuum chamber; at each checkpoint, different samples were investigated).

The morphology of the whiskers was observed on high-resolution SEM micrographs. Fig. 5 presents the samples that spent 250 h in a vacuum, and they were again investigated after 3 weeks at ambient conditions. An interesting phenomenon was revealed that the end part of the whiskers had an unusual block-like structure with a totally plain surface, while at the root of the whiskers, they had a twisted body with grooves, which is the more usual whisker morphology (Fig. 5a-d). According to the build-up of the whiskers, the block-like part had to grow first in the vacuum and later the twisted part in the ambient conditions while the samples were waiting for further morphological investigations. Similar whisker shape differences between vacuum- and ambient-grown whiskers were found in [19,22]; however, the difference was not as significant as in our case.

Only the presence of oxygen was the major difference between the storage conditions in the vacuum test and later keeping the samples in ambient atmosphere, so the morphological differences of the whiskers were indeed in connection with it.

TEM lamellae were prepared from a block-like Sn whisker to study its inside structure. The results are presented in Fig. 6. The body of the whisker was marked by a blue dashed line inside the Pt coating (Fig. 6a). According to SAED measurements (Fig. 6b), the whisker was a single crystal, and the Sn matrix had (220) and (101) orientations. Interestingly, in the body of the whisker, darker inclusions were barely visible with $\sim 50\ \text{nm}$ diameter in Fig. 6a. The high-angle-annular dark-field (HAADF) STEM micrograph and the EDS maps in Fig. 6c proved that the inclusions contained Cu.

The structure of an inclusion (marked by M1 in Fig. 6a) is more observable in the HR TEM micrographs (Fig. 6d). Further EDS line

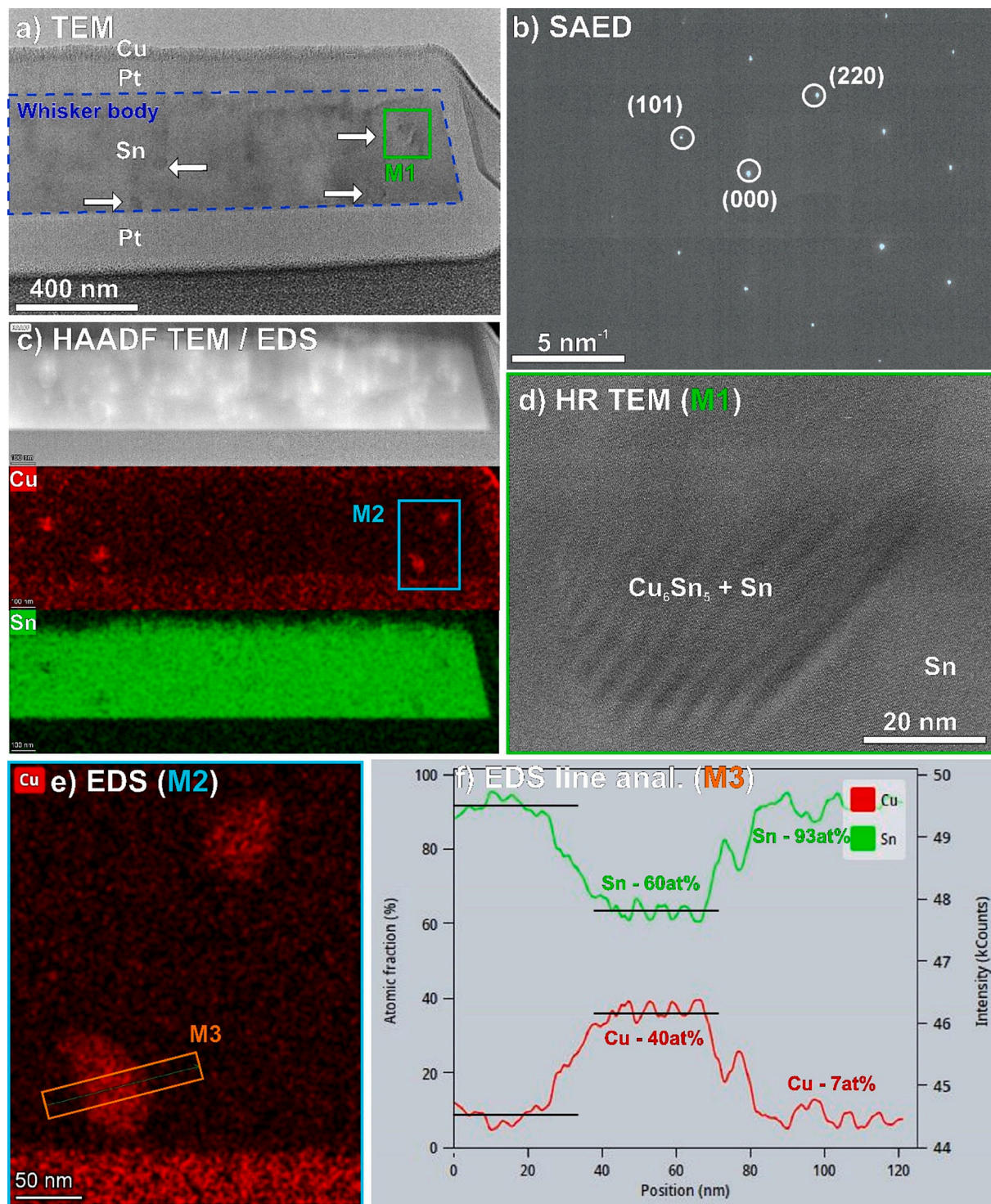


Fig. 6. TEM analysis of block-like Sn whisker: a) BF TEM micrograph of the whisker; b) SAED pattern; c) HAADF STEM and EDS maps of Sn and Cu recorded from the whisker; d) HR TEM of M1 area; e) EDS map of Cu of M2 area; f) EDS line analysis of M3 recorded from the marked region in (e).

analysis of an inclusion (marked by M3 in Fig. 6e) revealed that its composition was close to the Cu_6Sn_5 , but it was not a pure Cu_6Sn_5 , it was more likely a mixture of Cu_6Sn_5 and Sn.

4. Discussions

4.1. Growth characteristics of the Sn whiskers

As mentioned above, the increase in the whisker statistics over time

was not totally monotonous since the test was a non-return type. However, overall, both the density and most frequent length of the whiskers showed a characterizable increase during the test. The whisker density (d) increase over time (t) can be described by the following power law (Fig. 4a):

$$d = 6.25 t^{0.33} \quad (1)$$

Eq. (1) matches with the model of Cu_6Sn_5 IMC layer growth at an Sn/Cu interface, which can be adequately modeled with the following

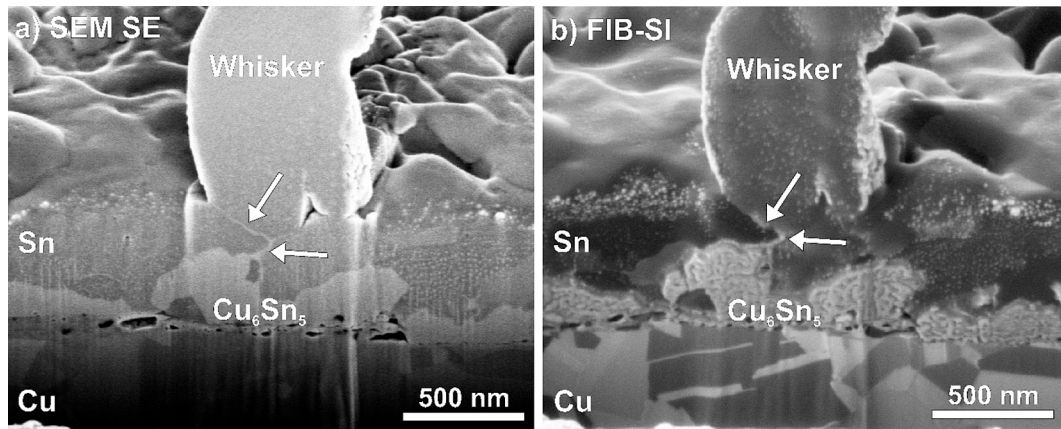


Fig. 7. FIB cross-section at the root of an Sn whisker (after 500 h test): a) SEM SE micrograph; b) FIB SI micrograph.

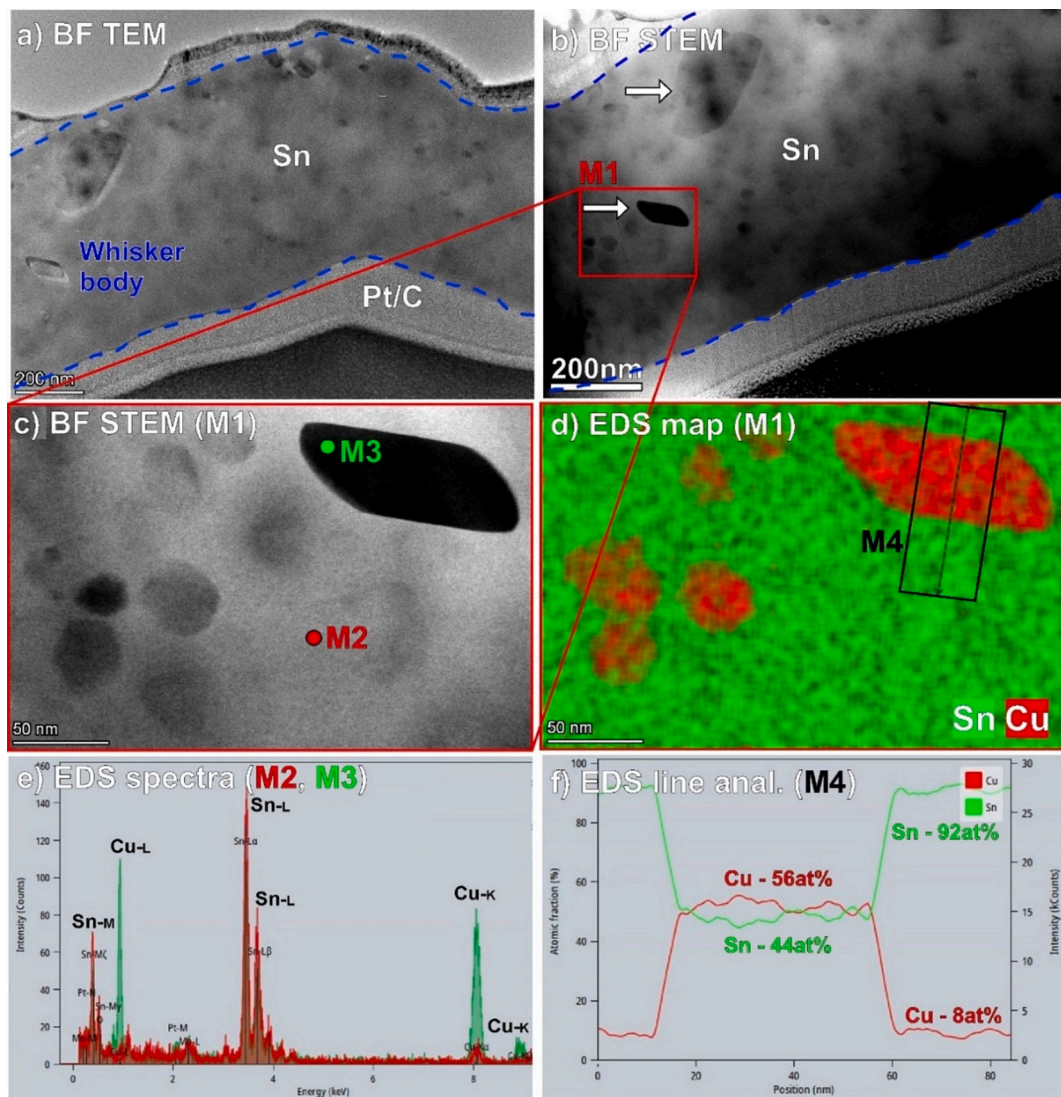


Fig. 8. TEM analysis of twisted Sn whisker: a) BF TEM of the whisker body; b) BF STEM of the whisker body; c) a zoom-in BF STEM of the whisker body (M1); d) EDS map of Cu and Sn of M1; e) EDS spectra of M2 and M3; f) EDS line scan analyzes of M4.

empirical power law [27]:

$$h = K t^n \quad (2)$$

where h is the thickness of the IMC layer, K is the coefficient of the IMC growth rate, and n is the time exponent. If $n = 1/3$, the interfacial IMC growth follows the parabolic law and is grain boundary diffusion-controlled, like in our case [28]. So, it suggested that in the thermo-

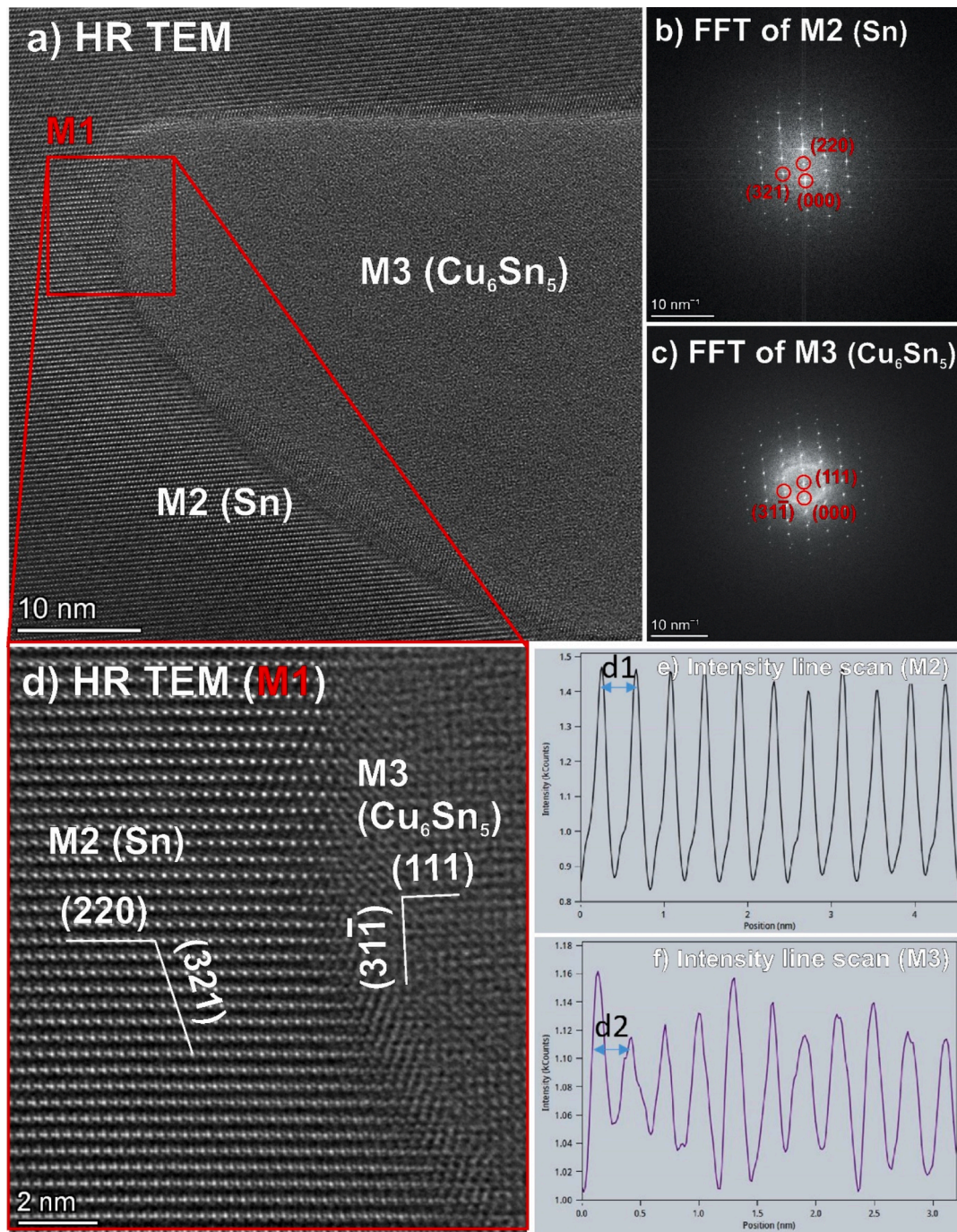


Fig. 9. HR TEM analysis of a large Cu_6Sn_5 inclusion and its surroundings: a) HR TEM micrograph of the investigated area; b,c) FFT diffractograms of M2 and M3 SAED of M2; c) SEAD of M3; d) HR TEM of M1; e, f) Intensity line scans extracted from M2 and M3 in (d), respectively.

vacuum conditions, the main influential factor of the Sn whisker growth was the mechanical stress caused by the Cu_6Sn_5 layer growth. However, after 500 h of the test, saturation is visible in the density growth, which means a decrease in mechanical stress.

Fig. 7 presents a FIB cross-section at the root of an Sn whisker to investigate the previous assumptions. The layer structure at the whisker root is well distinguishable and observable in Fig. 7, which shows large wedging Cu_6Sn_5 IMC grains (have a light gray color) directly under the whisker that almost reached the root of the whisker. These large wedging Cu_6Sn_5 IMC grains initiated the mechanical stress, which caused the growth of the whisker. Penetration lines are visible from the left Cu_6Sn_5 IMC grain (marked by white arrows), which could explain

the origin of the Cu_6Sn_5 inclusions in the body of the whisker, as it was observed in Fig. 6.

The most frequent length (l) showed linear but very slow growth in time with the following function (Fig. 4b):

$$l = 1.13 + 2.65 \cdot 10^{-4} t \quad (3)$$

The whiskers grew relatively fast, close to their maximum length, but their length increase did not stop completely during the test. The characteristic of the most frequent length can be explained by the fact that mechanical stress relaxation occurs more with an increase in density than in the length of whiskers. There is a rapid mechanical stress relaxation effect at the onset of whisker growth, which changes in a slow

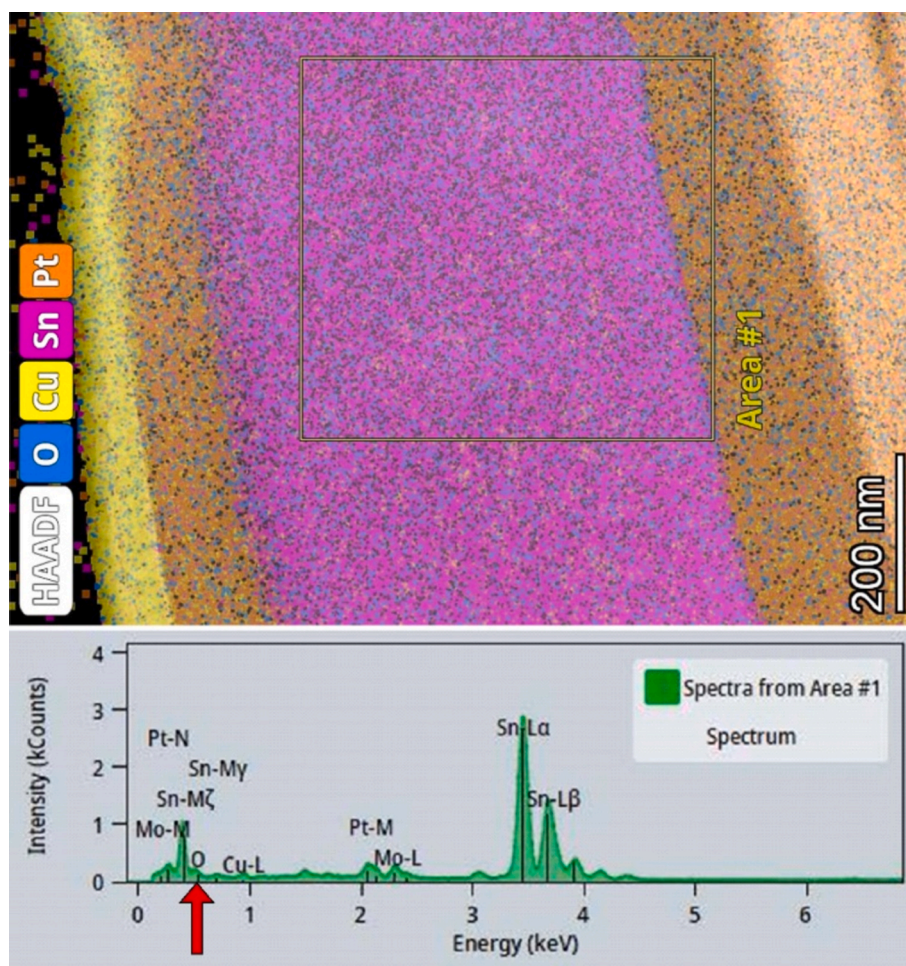


Fig. 10. EDS map (Sn, Cu, O, and Pt) of the twisted whisker and the related EDS spectrum of area #1.

and constant growth rate when the mechanical stress is lower.

Previously, we executed a similar Sn whisker study [26] on the same samples; the difference was only that we used an ambient atmosphere, so it is worth comparing the results of the studies. Similar whisker density saturation was observed around 500 h in ambient conditions as well due to the consumption of the Sn layer by the Cu_6Sn_5 layer development. However, the number of the developed Sn whiskers was lower, only ~ 40 pcs./ $1\text{E}4 \mu\text{m}^2$ after the 1000 h. This agreed with the findings of Suganuma et al. [17] and Jo et al. [18], who reported more whiskers in vacuum conditions than in ambient. This was caused mostly by the lower number of short nodule-type whiskers in ambient conditions than in vacuum conditions. In contrast, whiskers grew much longer in ambient conditions than in vacuum conditions. Even the average filament whisker length was approximately $45 \mu\text{m}$, and several $200\text{--}400 \mu\text{m}$ long whiskers were detected in ambient conditions after 1000 h [26]. Similar results regarding the longer filament whisker at constant ambient conditions were reported in the case of Sn-Cu layer systems [15,16]. This contradicts the results of Sn-(Alloy42/Si/ Al_2O_3) layer systems aged by thermal cycling, where longer whiskers were found in a vacuum than in ambient conditions [17–19], which highlights the different growth mechanisms in the case of different material systems and storage conditions.

4.2. TEM analysis of the Sn whiskers

Two additional TEM lamellae were prepared from the whiskers to study further the differences between the vacuum and ambient conditions grown parts. Fig. 8 shows the TEM analysis of a twisted Sn whisker.

The body of the whisker was marked by a blue dashed line inside the Pt coating (Fig. 8a and b). The contrast differences in the bright-field (BF) (S)TEM micrographs (Fig. 8a–c) indicated that this whisker body also contained different elements. Several smaller and bigger ($\sim 40\text{--}200$ nm) inclusions are visible in the whisker (Fig. 8b and c). The EDS map of Cu and Sn extracted from the M1 area (Fig. 8d) showed that most of the inclusions contained large amounts of Cu, like in the case of the block-like whisker in Fig. 6d. The EDS composition measurements of M2 and M3 showed that the whisker body contained Cu and Sn; some Pt was also detected from the protective cover of the whisker (Fig. 8e). The EDS line analysis (Fig. 8f) indicated that the composition of the inclusions (56 at % Cu and 44 at % Sn) is very close to the Cu-Sn at% ratio of Cu_6Sn_5 IMCs.

High-resolution (HR) TEM analyses (Fig. 9) were carried out to investigate the large Cu inclusion and its surroundings (M3) in Fig. 8c. The HR TEM micrographs in Fig. 9a and d nicely show the crystal structure difference between the Cu_6Sn_5 inclusion and the surrounding area. The fast Fourier transformed (FFT) diffractograms of M2 and M3 proved that both the Cu_6Sn_5 inclusion and the surrounding area were single crystals (Fig. 9b and c). The lattice spacing measurements (Fig. 9e and f) and FFT diffractogram analysis of M2 and M3 areas showed that the Sn matrix had orientations (220) and (321), while the Cu_6Sn_5 inclusion had (111) and (31–1).

Fig. 10 presents an EDS map of Sn, Cu, O, and Pt extracted from the full cross-section of the twisted whisker (in Fig. 8) and the related spectrum for area #1. Contrary to the results from the literature [18,22], no detectable amount of oxygen was found on the surface of the twisted whisker. This means that the SnO_x on the surface of the whiskers could be only some atomic layer.

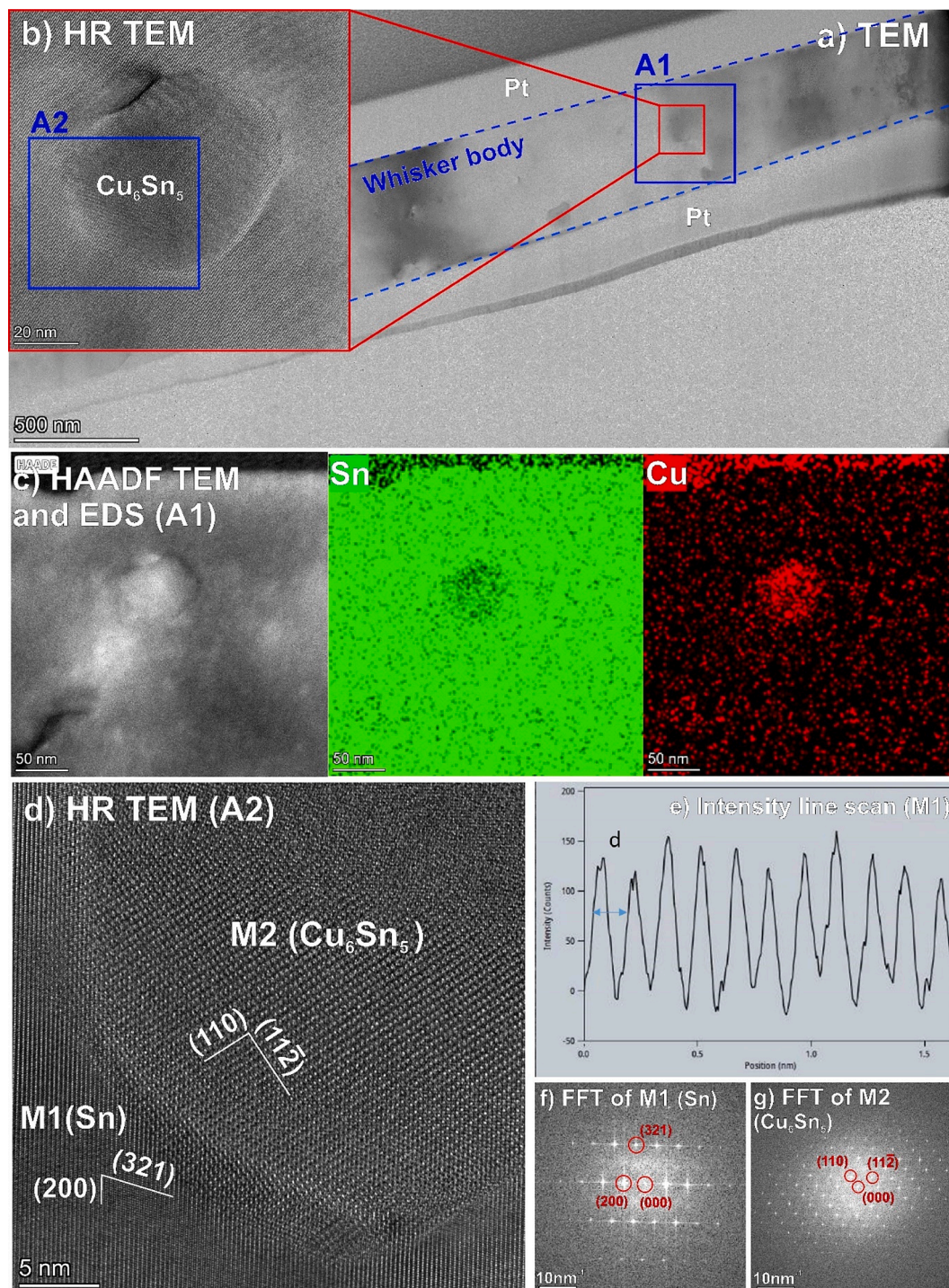


Fig. 11. TEM analysis of block-like Sn whisker #2: a) BF TEM micrograph of the whisker; b) HR TEM micrograph of a Cu_6Sn_5 inclusion; c) HAADF STEM and EDS (A1) map of Sn and Cu of area A1; d) HR TEM of area A2; e) Lattice spacing of M1; f, g) FFT diffractograms of M1 and M2, respectively.

Fig. 11 presents a further TEM analysis of a block-like Sn whisker. The body of the whisker was marked by a blue dashed line inside the Pt coating. It also contained inclusions, which have a darker contrast in the TEM micrograph (Fig. 11a). The HR TEM micrograph in Fig. 11b shows the structure of inclusion, which was chosen for further analysis. Fig. 11c presents the HAADF STEM and EDS maps of Sn and Cu of the investigated area A1 in Fig. 11a. The EDS results showed that this inclusion was also Cu_6Sn_5 (54 at% Cu and 42 at% Sn). The analysis of the M1 and M2 in the HR TEM micrograph (Fig. 11d) using line scan (Fig. 11e) and FFT diffractograms (Fig. 11f and g) also confirmed that

the inclusion is Cu_6Sn_5 . The orientations of the Sn matrix were (200) and (321), and the Cu_6Sn_5 matrix had orientations (110) and (112).

4.3. Differences between the twisted and block-like Sn whiskers

Comparing the results of the twisted and the block-like whiskers, it can be concluded that the twisted whiskers contained more Cu_6Sn_5 inclusions than the block-like whiskers. It was approximately 4–5 at.% in the block-type whiskers and approximately 8–12 at.% in the twisted whiskers (measured on the bulk TEM samples). The Cu_6Sn_5 content of

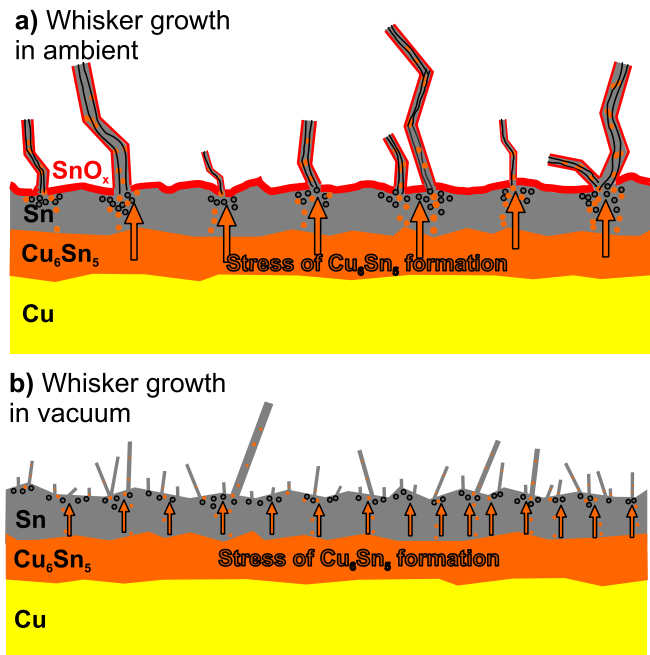


Fig. 12. Whisker growth: a) in ambient conditions; b) in vacuum conditions.

the whisker body is not rare in the case of very thin Sn layers, and it can be explained by the interface flow mechanism. The extremely high stress caused by the Cu_6Sn_5 IMC layer growth in the thin Sn layer could initiate the interface flow mechanism between the Sn layer and the Cu_6Sn_5 IMC layer when the Sn and Cu (or Cu_6Sn_5) atoms (or molecules) can flow along a fluid-like viscous layer at the interface of Sn film and the Cu_6Sn_5 IMC layer. They constantly migrate in this viscous layer towards the lower stress regions, which are the roots of the whiskers, since whisker growth is a stress relaxation mechanism [29]. No direct correlation was found between the Sn and Cu_6Sn_5 crystals' orientations and the shape of the whiskers. However, it has to be noted that the crystal structure of the block-like whiskers had a tighter grid structure (the Sn atoms were closer to each other) than the twisted ones.

In the literature, the formation of the twisted whisker with the grooves on the body was explained by the grain boundary cracking phenomenon at the root of the whiskers [17]. It means that the sharp and hard SnO_x nailings at the side of the crack scratched the grooves and bent the whiskers. Jo et al. [18] gave a very similar explanation. Both teams worked with electroplated Sn aged by thermal cycling in a vacuum and ambient conditions. In the present research, we did not find evidence of grain boundary cracking; however, our samples and aging conditions were different than in [17,18]. Horvath [30] proved that the contaminant inclusions (Cu, Ag, Bi, etc.) in the body of the whiskers have a major role in the formation of twisted whiskers. That is why more nodule-type twisted whiskers usually grow from SnAgCu alloys than from pure Sn. The accumulated inclusion can even cause sub-grain formation in the whisker body, although we did not observe this phenomenon in this study. The sub-grain formation in the whisker body could cause the growth of whisker branches from the base whisker [30]. Horváth observed the same grooved surface of the whisker branches as the base part, but no sign of grain boundary cracking was visible at the root of the investigated whisker branches [30].

So, it can be concluded that the grain boundary cracking at the whisker roots can cause the growth of twisted whiskers with the grooves in ambient conditions, but not exclusively. In our case, the structural differences of the Sn whiskers grown in vacuum and ambient conditions were probably more related to their different Cu_6Sn_5 content. The development of block-like Sn whiskers in a vacuum might be caused by the lower amount of Cu_6Sn_5 inclusions in their body and by the

relaxation of the whisker surface driven by surface energy reduction [22]. The development of the twisted whiskers with the grooves in the ambient condition might be caused by the higher amount of Cu_6Sn_5 inclusions in their body and the grooves related to the surface oxidation of the whisker, as was found by Liu et al. [22], concluded, that grooves on the ambient-grown whiskers are inherited from the whisker nucleus and are preserved by the surface oxide film. However, we could not verify it during the study.

It was also interesting how the lack of air could cause a difference in the amount of the Cu_6Sn_5 inclusions in the vacuum- and ambient-grown whiskers. Fig. 12 summarizes the supposed difference between whisker growth in vacuum and ambient conditions in Sn-Cu layer systems. In the case of ambient conditions, a nearly contiguous SnO_x layer formed on the surface of the Sn layer (Fig. 12a). This oxide layer generally blocked the relaxation of the stress generated by the Cu_6Sn_5 formation. Stress relaxation and whisker growth could occur mostly only at the discontinuity points of the oxide layer (crack/holes) [5].

This resulted in the accumulation of stress at these discontinuity points, causing the growth of less but longer whiskers (Fig. 12a), as was observed in [26]. Furthermore, the locally larger stress indicated stronger interface flow (Fig. 12a), which resulted in the migration of more Cu_6Sn_5 into the whiskers than in vacuum conditions, as was observed in our study. In the case of vacuum conditions, the oxide layer could not form on the surface of the Sn layer (Fig. 11b), so stress generated by the Cu_6Sn_5 formation could relax much more uniformly and on a much larger surface than in the case of the ambient conditions. This resulted in the growth of much more but shorter Sn whiskers with fewer Cu_6Sn_5 inclusions than in ambient conditions.

5. Conclusions

Sn whisker growth was investigated from submicron Sn layers on Cu substrates in thermal vacuum conditions to compare the growth differences in ambient and vacuum (space) conditions. The main findings are the following:

- Several Sn whiskers were detected on the submicron Sn layer already after 75 h of thermo-vacuum test. The density of whisker growth followed a parabolic law with $n = 1/3$, proving that the main inducing factor of the whisker growth was the IMC layer growth between the Sn and Cu substrate.
- The vacuum condition developed approximately 50 % more but 50–70 % shorter whisker than that in ambient conditions. Furthermore, the morphology of the whiskers considerably differed. In the vacuum condition, Sn whiskers had a block-like body with a totally plain surface, while in the ambient condition, Sn whiskers had a twisted body with grooves.
- TEM investigations revealed a large amount of Cu_6Sn_5 inclusions in the body of the whiskers, which could get into the whiskers by the interface flow mechanism between the Sn layer and the Cu_6Sn_5 IMC layer. The twisted whiskers (in ambient conditions) contained approximately twice as many Cu_6Sn_5 inclusions as the block-like whiskers (in vacuum conditions). It suggests that the role of Cu_6Sn_5 extends beyond merely providing a driving force.
- Only a weak correlation has been found between the crystal structure and the shape of the whiskers, namely that the crystal structure of the block-like whiskers had a tighter grid structure (the Sn atoms were closer to each other) than the twisted whiskers.
- The lack of an oxide layer in the vacuum allowed better stress relaxation and more starting points of whisker growth for the Sn layer, which resulted in more but shorter whiskers than in ambient conditions. In addition, the lower stress level took less Cu_6Sn_5 inclusion in the body of the whiskers, which could cause the development of the block-like Sn whiskers in the vacuum.

CRedit authorship contribution statement

Balázs Illés: Writing – original draft, Supervision, Resources, Project administration, Methodology, Conceptualization. **Agata Skwarek:** Writing – original draft, Project administration, Funding acquisition, Conceptualization. **Tamás Hurtony:** Investigation, Formal analysis, Conceptualization. **Oliver Krammer:** Validation, Software, Investigation. **Bálint Medgyes:** Methodology, Investigation, Formal analysis. **Krzysztof Szostak:** Methodology, Investigation, Formal analysis. **Gábor Harsányi:** Visualization, Validation, Investigation. **András Kovács:** Writing – review & editing, Visualization, Validation, Software. **Béla Pécz:** Writing – review & editing, Validation, Methodology, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was carried out under a program of and funded by the European Space Agency, entitled “Current Capacity and Effects of Vacuum of Tin Whiskers”, ESA AO/1-11458/22/NL/FE. The authors acknowledge the support of M. Lekka and P. López (CIDETEC) in providing the Cu substrates and of L. Illés (HUN-REN) in preparing the TEM specimen. A.K. acknowledges the support of the MTA Distinguished Fellowship Programme 2024. B.I. and B.M. acknowledge the support of the National Research Development and Innovation Office – Hungary (NKFIH), to projects K 145966 and FK 138220, respectively. The view expressed herein can in no way be taken to reflect the official opinion of the European Space Agency.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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