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Combinatorial Preparation and Electrochromic Investigation of Metal Oxide Mixtures

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The physical, chemical and structural properties of the cutting-edge materials are strongly dependent on their composition. The common procedure to reveal the properties of concentration dependent phases is the preparation of numerous two (or more)-component samples, one for each C(a)/C(b=1-a) composition, and the investigation of these individuals. This is a low efficiency procedure that costs enormous time of man and machine. Contrarily, using the combinatorial material synthesis approach, materials libraries can be produced in one experiment that contain up to several hundreds or thousands of samples on a single substrate. In order to identify optimized material structures in an efficient way, adequate automated sub-millimeter-spot material characterization tools have to be applied. These methods can help us to search more efficient advanced functional materials for micro-, nano- and optoelectronics, energy converters (solar cells) or different (optical or gas) sensor systems.

TiO₂-SnO₂ investigation

We searched [1] the optimal composition of reactive magnetron-sputtered combinatorial mixed layers of Titanium oxide and Tin oxide (TiO_2 -SnO₂) for electrochromic purposes.

Spectroscopic Ellipsometry (SE) is an optical characterization technique with high-accuracy. The combinatorial approach used to investigate mixed metal oxides has several advantages, Fried et al. [Fried, M.; Bogar, R.; Takacs, D.; Labadi, Z.; Horvath, Z.E.; Zolnai, Z. Investigation of Combinatorial WO₃-MoO₃ Mixed Layers by Spectroscopic Ellipsometry Using Different Optical Models. *Nanomaterials* **2022**, *12*, 2421 https://doi.org/10.3390/nano12142421] have used SE (which is a fast, cost-effective, and non-destructive method) for the investigation and mapping of WO₃-MoO₃ mixed layers after sputtering. Different optical models, such as EMA and 2T–L, have been used to achieve the composition map and thickness map of our Ti-Sn oxide combinatorial layers.

We mapped and determined the composition and optical parameters using Spectroscopic Ellipsometry (SE). Different optical models, such as 2-Tauc–Lorentz multiple oscillator model (2T–L) or the Bruggeman Effective Medium Approximation (BEMA) were used to obtain the composition maps and the thickness of the sample. Scanning Electron Microscopy (SEM) with Energy-Dispersive X-ray Spectroscopy (EDS) was used to verify the SE results. We also compared the performance of diverse optical models. It was shown that in the case of molecular-level mixed layers, 2T–L is better than an EMA based optical model. By using SE, the electrochromic efficiencies of mixed metal oxides (TiO₂-SnO₂) deposited by reactive sputtering were also mapped, too, see Fig. 1.



Fig. 1 (a) The imaginary part of the refractive index (k Amplitude) as a function of time for highly conductive Si in the liquid cell during coloration (time-scan, simple 2-layer Cauchy model). From 0–4 min, there is low absorption, however, from 4–8 min, there is a growing absorption; (b) Map of the k parameter after coloration (simple 1-layer Cauchy-model). From Ref. [1]

The coloration process was followed in situ by SE at the center point of the mixed metal oxide – highly conductive Si sample. We mapped the colorized layer using a simple one-layer Cauchy dispersion optical model after the coloration process. For the Cauchy model, the k Amplitude (extinction) parameter has been considered a good indicator of the coloration efficiency, as it is shown in Fig. 1 b. The maximum k value shows that the optimal composition is at (30%) TiO₂– (70%) SnO₂. See Table I.

| X (cm) | k Amplitude (Error \pm 0.005) | |
|--------|---------------------------------|--|
| -3.5 | 0.0002 | |
| -3 | 0.0025 | |
| -2.5 | 0.044 | |
| -2 | 0.004 | |
| -1.5 | 0.015 | |
| -1 | 0.025 | |
| -0.5 | 0.056 | |
| 0 | 0.041 | |
| 0.5 | 0.092 | |
| 1 | 0.105 | |
| 1.5 | 0.075 | |

Table I The k Amplitude vs. Position at the center line after the colorization in the dry state.

WO₃-MoO₃ investigation

We prepared W_xMo_{1-x} oxide thin film system (where 0 < x < 1) by reactive magnetron sputtering onto ITOcovered glass and the optimal composition for the best coloration efficiency (CE) was determined [2]. Continuous composition range was deposited in one experiment on a single substrate with combinatorial material synthesis approach, the samples represented the full composition range of the binary MoO_3/WO_3 system. Our nondestructive composition determination method [3] was used for the same layers deposited on silicon substrates using spectroscopic ellipsometry.



Fig. 2 WO3-MoO3 layers on ITO-covered glasses and Si-probes. From Ref. [2]



Fig. 3 Layer thickness and Mo ratio vs sample position from SE (left) The RBS and SE results together (Right) From Ref. [2]



Fig. 4 Measured and simulated (fitted) RBS spectra from the W-rich side; (a), from the Mo-rich side; (b), and from near the centre position; (c) of the sample, together with a composition-map along a line as evaluated from RBS data (d). From Ref. [2]

The best determination of the optimal composition for the best CE, the layers were deposited onto ITOcovered glass. The composition map and thickness map were measured on the Si-probes by SE, see Fig. 2 and 3. We checked the resulted compositional map on the Si-probes by using Rutherford Backscattering Spectrometry (RBS), see Fig. 4.

The Coloration Efficiency η is given by following equation:

 (\mathbf{T})

$$\eta(\lambda) = \frac{\Delta OD(\lambda)}{q/A} = \frac{\ln\left(\frac{T_b}{T_c}\right)}{Qi}$$

where Q_i is the electronic charge inserted into the electrochromic material per unit area, ΔOD is the change of optical density, T_b is the transmittance in the bleached state, and T_c is the transmittance in the colored state. The unit of a Coloration Efficiency is cm² C⁻¹.

(1)



Fig. 5 Transmission electrochemical cell during-electrochromic-experiments by SE to measure coloration efficiency

The Coloration Efficiency (CE) has been determined in a transmission electrochemical cell, see Fig. 5. The cell was filled with 1M lithium perchlorate (LiClO₄) / propylene carbonate electrolyte. A 5 mm width masked (metal-oxide-free) stripe of the slides remained above the liquid level allowing direct electric contact onto the ITO layer. A Pt wire counter electrode was placed into the electrolyte alongside with a reference electrode. This arrangement was a fully functional electrochromic cell. The applied current was controlled through the cell using a Farnell U2722 Source Measurement Unit (SMU). Constant current was registered through coloration and bleaching cycles of the electrochromic layer. Simultaneous spectral transmission measurements were performed by using the Woollam M2000 spectroscopic ellipsometer into transmission mode.

Transmittance was measured in the spectral range of 400–800 nm. CE values were determined at every composition from the measured relative transmission vs. input charge curves. We used eq. 1 to determine CE at 5 wavelengths (400-800 nm visible range) for every compositional position using the relative transmission curves and fitted exponential curves. The determined results, CE vs. composition and vs. wavelength are shown in Fig. 6.



Fig. 6. CE vs. composition curves clearly show that a characteristic maximum of CE exists at the 60% Mo fraction. Furthermore, this maximum is present throughout the (400-800) nm visible spectral range, and its relative intensity increases towards the red end of the spectrum. From Ref. [2]

Coloration efficiency data were evaluated from the primary data plotted against the composition displayed a characteristic maximum at around 60% MoO3. Determination of the place of the maximum was possible at 5% accuracy due to the combinatorial approach, see Fig. 6.

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Spatial distribution of photoexcited electrons and holes in Cu₂O/Au multicomponent nanoparticles

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Combining the ability of semiconductor nanoparticles (NPs) to produce photogenerated electrons and holes, with noble metals capable of enhancing the spatial separation of charge carriers gained tremendous attention in material science in the recent decades. Hence, countless studies have been reported focusing on the synthesis and characterization of the photophysical and photochemical properties of multicomponent semiconductor/metal NPs. Cuprous oxide (Cu₂O) is considered an outstanding candidate for the semiconductor component, owing to its outstanding properties including its high charge carrier concentration, large exciton binding energy, non-toxicity, and its band gap being active in the visible and near UV range.¹⁻³ In spite of the excessive research of multicomponent NPs, to reveal insight into the photogenerated charge carriers' spatial distribution as well as its influence on the photophysical and photochemical properties in Cu₂O/Au multicomponent NPs with well-controlled morphology remained unexplored. In this paper, wet-chemical syntheses were elaborated to realize pristine Cu₂O NPs (Figure 1a-c) as well as their heterostructured counterparts containing Au in two different arrangements: (i) individual gold nanorods (AuNRs) were embedded inside the Cu₂O NPs' center (Figure 1d-f), and (ii) gold nanograins (AuNGs) were grown onto the surface of the Cu₂O NPs with the same atomic quantity (Figure 1g-i). All of the three NP systems possessed octahedral shape with ca. 140 nm base edge length and identical Cu₂O content. The high morphological control enabled to reveal, how the presence and position of the Au affect the photo-physicochemical properties of the pristine Cu₂O nanooctahedra.⁴



Figure 1. Representative SEM images of the nanoparticles with high magnification TEM images in the insets, as well as atomic-resolution TEM images and elemental distribution EDS maps for the pristine (a-c), the AuNG-decorated (d-f), and the AuNR-embedded Cu₂O nanooctahedra (g-i), respectively.⁴

The octahedral-shaped Cu₂O enclosed with $\langle 111 \rangle$ facets has been found to possess the highest catalytic performance among the different morphologies.¹ However, the restrained mobility of the photoexcited charge carriers associated with the vast defect states of metal-oxide semiconductors limits their potential in catalytic applications. Direct contact with noble metals provides a platform to overcome this limitation by separating the photoexcited electrons and holes. The aim of the study was to untangle the distribution of the charge carriers photoexcited in the semiconductor compartment of the NPs. To exclude the presence of hot electrons originating from the plasmonic nature of Au, a low-energy UV flashlight with a wavelength of around 400 nm served as an excitation source, that is off-resonant with the plasmon resonance of Au. In this case, the dominant charge carrier generation process is addressed to the band-to-band transition in Cu₂O.

To shed light on the nanoparticles' optical properties, absorption and excitation spectra in the UV-Vis-NIR region as well as photoluminescence (PL) spectra and time-correlated single photon counting (TCSPC) were recorded at 0.5 mM Cu₂O concentration for each of the three nanoparticle model systems (Figure 2). For the multicomponent NPs, both the decrease of the PL intensity and the faster decay of the fluorescence lifetime indicate an enhanced charge carrier separation compared to that of the pristine Cu₂O.



Figure 2. Extinction (a), absorption (b), and PL (c) spectra as well as TCSPC (d) of the multicomponent NP model systems at 0.5 mM Cu_2O concentration for each measurement.⁴

From the absorption spectra of the pristine Cu_2O NPs, the band gap energy was determined by the Tauc-plot and resulted to be 2.15 eV, which is in-line with the reported band-gap.¹ Additionally, the relative work functions were determined by single-point Kelvin probe: relative to the pristine Cu₂O nanooctahedra, -150 meV and +145 meV contact potential differences were measured for the AuNG decorated and for the AuNR-embedded Cu₂O nanooctahedra, respectively. Comparing the valence band maxima (determined by XPS) of the different Au/Cu₂O NPs, 430 meV larger binding energy was measured for the AuNR-embedded particles, indicating a higher valence band maximum for the AuNG decorated model system. The work function of the $\langle 111 \rangle$ facets of Cu₂O was experimentally determined by Tan et al (4.80 eV).⁵ Previous studies showed, that the work function of Au NPs shows a size-dependent nature in the 3-10 nm size regime, attributed to their electrostatic interaction with the adjacent materials: upon decreasing the size of the Au particle, its Fermi level changes from 5.3 eV (bulk Au) to 3.6 - 3.8 eV (7 nm Au grain on Si/SiO₂ surface).⁶ Based on the above considerations, the energy landscape was proposed (Figure 3). In the case of the AuNG decorated model system, the work function decreases at the Cu₂O/Au interface, resulting in a downward band bending upon the equilibration of the Fermi levels. Consequently, a Schottky barrier forms for the holes, thus, the electrons and holes are accumulated in the AuNGs and the Cu₂O surface, respectively. In contrast, the equilibration of the Fermi levels in the AuNR-embedded model system results in an upward band bending, resulting in a Schottky barrier for the electrons. Consequently,

the electrons and holes are accumulated in the Cu_2O and the AuNR, respectively. This implies a fundamentally different charge separation process in the engineered multicomponent particles dictating the avalability of the electrons and holes in a photocatalytic reaction.



Figure 3. Tauc plot of the pristine Cu_2O NPs served to determine the bad gap energy (a). Determination of the contact potential differences by single-point Kelvin probe (b). Valence band spectra of the multicomponent NPs measured by XPS (c). Schematic energy landscape diagram comparing the AuNR-embedded (*i* and *ii*) and the AuNG-decorated (*iii* and *iv*) multicomponent NPs before and after the contact, respectively.⁴

This hypothesis was also tested in the photocatalytic degradation reaction of methyl orange. Decoration of the Cu_2O nanooctahedra with small Au nanograins enabled enhanced activity and resistance against photocorrosion compared to the AuR/Cu₂O and pristine Cu₂O NPs.

In conclusion, it can be declared that the presence of gold in Cu_2O nanooctahedra significantly improves the photocatalytic activity, and provides a platform to utilize a low-power UV illumination, in which condition the pristine Cu_2O nanooctahedra is inactive. Furthermore, it has been shown that besides the presence, the position of gold is also crucial from the application point of view. The morphological arrangement of the nanograin-decorated model system provides the simultaneous availability of both charge carriers, favoring the photocatalytic performance as well as the photostability of the nanoparticles.

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Helium ion beam-induced luminescence from defect centers in Al₂O₃

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Al₂O₃ is a promising scintillator for energetic charged particle (e.g. He⁺, H⁺) detection due to its luminescence emitted in the near UV-visible spectral range by impurities or stable defects introduced into the wide bandgap material [1]. On the other hand, ion beam-induced luminescence (IL) is a sensitive and effective analytical method to study and optimize scintillator-based particle detector structures. In this work, the IL light emission of α -Al₂O₃ was induced by a 1.5-MeV He⁺ ion beam and measured as a function of irradiation time (ion fluence). He⁺ projectiles were used to simulate the effect of the daughter product in the ¹⁰B(n, α)⁷Li reaction, when thermal neutrons are detected via their conversion to 1.47-MeV α and 0.84-MeV Li⁺ particles which than generate IL emission in a scintillator. He⁺ beam-induced IL spectra were recorded in the wavelength range of 200 nm - 1100 nm. Two prominent emission bands were identified and recognized as the well-known F/F⁺ centers [2, 3] related to oxygen vacancy defects with two electrons/one electron captured.

In a detector structure, sufficient sensitivity as well as reliable correlation between the number of α -particles (the α -flux) and the α -induced IL intensity can be achieved if the response of the scintillator is fairly intense and stable in time. In order to see the effect of initial concentration of F/F⁺ centers on the IL response of Al₂O₃, both unimplanted and pre-implanted sapphire samples were measured by the IL technique. Pre-implantation was performed by 2.8-MeV N⁺ ions in the fluence range 5×10¹³ - 5×10¹⁴ N⁺/cm², resulting in high defect densities in the uppermost 2 µm region of Al₂O₃. He⁺-IL experiments and N⁺ ion irradiation were performed by the EG-2R Van de Graaff accelerator at the Institute for Particle and Nuclear Physics, HUN-REN Wigner Research Centre for Physics in Budapest.



Figure 1. 1.5-MeV He⁺ beam-induced IL spectra of the F and F⁺ centers at a fluence of 1.2×10^{16} He⁺/cm² for unimplanted Al₂O₃ (left), and for a pre-implanted Al₂O₃ sample (right) irradiated with 2.8-MeV N⁺ ions to a fluence of 5×10^{14} N⁺/cm² before the IL measurement.

Fig. 1 shows IL spectra of α -Al₂O₃ after 1.2×10¹⁶ He⁺/cm² exposure, both without and with N⁺ pre-implantation. Spectra are shown after appropriate background subtraction and intensity

normalization, taking into account the instrument function along the optical path and the quantum efficiency of the CCD camera. Solid lines (red and blue) show Gaussian fits of the two prominent IL bands. The extracted peak positions for the F and F^+ centers are 2.99 eV and 3.79 eV, while full widths at half maximum (FWHM) are 0.42 eV and 0.35 eV, respectively. These peak energies and widths agree well with previously reported room temperature values [2, 3]. Strikingly lower F-center related peak appears for the pre-implanted sample compared to the one with no pre-implant.



Figure 2. Evolution of 1.5-MeV He⁺ beam-induced IL intensity of the F and F⁺ centers vs. the He⁺ irradiation fluence. for unimplanted Al_2O_3 (left), and for a pre-implanted Al_2O_3 sample (right) irradiated with 2.8-MeV N⁺ ions to a fluence of 5×10^{14} N⁺/cm² before the IL measurement.

For a sapphire sample without N⁺ pre-implantation, the emergence of both IL peaks starts after the He⁺ ion beam switched on, see Fig. 2. Toward higher fluences, a sublinear increase of the F and F⁺ center related IL intensity vs. He⁺ fluence occur. Nevertheless, for the F⁺ center a monotonous intensity increase can be seen, while for the F center the IL yield saturates after an exposure of about 5×10^{15} He⁺/cm². The increasing IL yield trend is due to He⁺ ion beam-induced defects, i.e., newly generated F and F⁺ centers of which concentration increases with the He⁺ fluence. On the other hand, for pre-implanted sapphire, relatively high F⁺-center related IL appears right at the beginning of the experiment and the IL yield saturates already above a fluence of 2×10^{15} He⁺/cm². No significant change, yet slight decrease for the F-center related IL was detected. A striking difference is the more pronounced split between the IL yields of the two centers for the pre-implanted sample as compared to the unimplanted one.

In summary, significantly higher F^+ center related IL can be detected in the low dose range of He⁺ ion irradiation for a sapphire sample with higher defect, i.e. F and F⁺ center concentration introduced by pre-implantation. Also, both for the F and F⁺ center, the IL yield vs. He⁺ fluence is more stable for higher defect concentrations. Differences in the F⁺ to F center related IL yield ratios can be related to different defect concentrations and compositions and related changes in the excitation and deexcitation processes. Our experiments can be utilized to optimize the material properties of Al₂O₃ for charged particle detection via IL emission.

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Electrochemical Corrosion of SAC305 solder alloy in 3.5% NaCl

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In this article, we deal with the electrochemical corrosion behavior of SAC305, in a 3.5% NaCl solution. In many cases, conflicting results are reported in the literature. In this article, we discuss system-specific problems and technical implementations of two types of electrochemical measurement methods, potentiodynamic polarization measurement and electrochemical impedance spectroscopy measurements, with the aim of being able to perform accurate, reproducible measurements.

The SAC305 solder alloy was received in flux-free solder wires form with a 1 mm diameter. To prepare the working electrode the solder wires were embedded in silicon tubes using epoxy resin for 2–3 days for complete hardening, leaving an exposed surface area of approximately 0.785 mm². Before electrochemical tests, the working electrodes were polished using silicon carbide (SiC) abrasive papers of grades ranging from 220 to 4000.

Polarization behaviour

The typical potentiodynamic polarization curves of SAC305 in 3.5 wt% NaCl solution is illustrated in Figure 1a, where the characteristic potential ranges are marked. Figure 1b-f show SEM images of SAC305 polarized to the indicated voltages. Since all polarization tests were implemented in aerated 3.5 wt% NaCl solution, the dissolved oxygen reduction reaction is the most common rate determining cathodic reaction (potential range I in Fig. 1a) when the corrosion of alloys takes place in nearly neutral solutions containing dissolved oxygen:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{1}$$

On further scanning from (E_{corr} , i_{corr}) points in the anodic direction until break potential (E_{break}) (potential range II in Fig. 1a), the corrosion current density is low, in the order of 10⁻⁷ A/cm², which is typical of passive metals. Dissolution of tin occurs at an extremely low rate followed by Sn(OH)₂ and Sn(OH)₄ formation which may dehydrate to SnO₂ and SnO respectively, according to Eqs. (2–7):

$$Sn \rightarrow Sn^{2+} + 2e^{-} \tag{2}$$

$$\operatorname{Sn+2OH^{-} \to Sn(OH)_{2} + 2e^{-}}$$
 (3)

$$Sn(OH)_2 \rightarrow SnO+H_2O$$
 (4)

$$Sn(OH)_2 + 2OH^- \rightarrow Sn(OH)_4 + 2e^-$$
(5)

$$SnO+2OH^{-}+H_2O \rightarrow Sn(OH)_4 + 2e^{-}$$
(6)

$$Sn(OH)_4 \rightarrow SnO_2 + 2H_2O \tag{7}$$

The passive range ends at E_{break} which is another crucial electrochemical parameter, it characterizes the solder capability of the protection of its passive film. The potential difference of $\Delta E = E_{corr}$ - E_{break} represents the local corrosion susceptibility.



Figure 1. a) Potentiodynamic polarization curves of the SAC305 solder alloys in 3.5 wt% NaCl solution, and b) – f) Scanning Electron Microscopy images of SAC305 alloy polarized to indicated voltage

Once reaching this value, passivity loss occurs and localized corrosion starts due to the presence of Cl⁻ ions initiated local corrosion spots which is assumed to be the main reason for the rupture of the passive layer, as a result, the oxide layer breakdown and repassivates, which is shown as fluctuations in the current density. With a further increase of anodic polarization from E_{break} , a sharp increase in current densities occurs until reaching the peak value at critical potential (E_{crit}), which is 5–6 magnitude larger than the corrosion current density (potential range III). Beyond E_{crit} the current density begins to drop and then the current density remains near independent of potential in the order of mA/cm² until the end of the polarization process (potential range IV), indicating the start of the corrosion product formation process. Fig. 1c-f shows the SEM-EDS results of the formed corrosion product in the case of SAC305 which showed a loose, mostly plate-like structure that no longer provides protection against corrosion. The elemental analysis of SEM confirmed that the corrosion product covering the surface is mostly Sn₃O(OH)₂Cl₂, as the Sn/Cl ratio was 1.6, which is very close to the theoretical Sn/Cl= 3/2 value.

$$3Sn+2Cl^{-}+4OH^{-} \rightarrow Sn_{3}O(OH)_{2}Cl_{2}+H_{2}O+6e^{-}$$
(8)

During recording of the complete polarization curve of SAC alloys, the current changes by 7 orders of magnitude. The maximum value of the current peak depends on the surface of the working electrode. At larger surface area the ohmic potential drop ($\Delta E=I\cdot R_{\Omega}$) resulting from the solution resistance may became significant, resulting distortion in current peak as demonstrated on Figure 2. When we want to accurately measure the entire polarization curve of such an electrochemical system, it is necessary to reduce the measurement error (distortion) resulting from the ohmic potential drop. The IR compensation options built into commercial potentiostats can mostly only be used by choosing a constant current range. This results in the fact that small currents in the vicinity of the corrosion potential cannot be determined, as they are values smaller than the current resolution. Another possibility is the use of the Luggin capillary, which can be used to reduce, but not completely eliminate, the distortion resulting from the ohmic potential drop. Further possibility is to reduce the working electrode.



Figure 2. Polarization curves of SAC305 solder alloy in 3.5% NaCl solution measured on different electrode surface areas. Electrodes: SAC305 wire with d=1mm ($A=0.00785cm^2$), reflowed from paste with d=1.8mm, ($A=0.025 cm^2$), and with d=18mm ($A=2.5cm^2$)

Monitoring the time dependence of corrosion behavior with a series of impedance measurements

Potentiodynamic polarization measurements provide valuable information on electrochemical kinetics, but the rate of metal dissolution at high applied potentials is also high, consequently one electrode is suitable only for one measurement. To examine the time dependence of corrosion, much smaller polarization signal must be used that does not significantly influences the natural course of corrosion over time. Electrochemical impedance spectroscopy is one of the options to monitor the time dependence of corrosion. For this purpose, we compiled a series of measurements in which the OCP and EIS measurements were repeated cyclically. In each case, a 30 min waiting time was used between recording individual impedance spectra, during which the OCP was measured.

The time-dependence of corrosion potential and polarization resistance of SAC305 in 3.5% NaCl solution is presented in Figure 3. Initially the E_{corr} value began to shift toward more noble values, approaching and reaching the E_{break} value. The driving force of the increase of corrosion potential in a neutral aerated 3.5% NaCl solution is one or a combination of two following changes: decrease of

the passivation current density, which means the formation of a thicker protective passive film; and depolarization of the cathodic curve, which happens when the pH is increased due to adsorption of OH⁻ anions on passive film. In the first few hours the polarization resistance is high, varying between 90 to 300 k Ω .cm², which is due to the stable passive oxide layer present on the surface of the solder alloys; there are no corrosion damage initially. The value of R_p may even increases slightly, based on which we can assume that the thickness of the oxide layer continues to increase even in the NaCl solution. The passive layer breakdown and the start of local corrosion are well indicated after 4-18 h of immersion, where a sharp drop of the E_{corr} was observed. When local corrosion starts, the polarization resistance decreases by 2 orders of magnitude. The major reason for the local corrosion damage in halide solution is the formation of water-soluble complexes with chloride. Pitting can occur during active dissolution if certain regions of the sample are more susceptible and dissolve faster than the rest of the surface, such as intermetallic particles such as Ag₃Sn and Cu₆Sn₅ which acts as the local cathode and accelerate corrosion in surrounding parts.



Figure 3. Local corrosion commencement monitoring and variation of polarization resistance and corrosion potential values for SAC305 solder alloy electrode. Measurement series were carried out in 3.5 wt% NaCl solution.

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TEM study of copper silicides

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Copper-silicides attracted considerable interest due to their wide range of applications. Cu₃Si is an important phase of the family. It is used in ultrapure silicon synthesis for photovoltaic and electric devices, as contact material in microelectronics and as catalyst for carbon nanowire and semiconductor production. Despite the importance of copper-silicides, their phase and structural relations are not entirely solved yet.

Due to their importance, we are studying the formation of copper-silicides in thin amorphous silicon (a-Si) films. A 10nm thick a-Si film was transferred to copper grid (Cu-grid) and heated insitu in a Philips CM20 transmission electron microscope. During the heating the Cu-grid acted as an unlimited source for the diffusion of metal into the s-Si film. We observed the η -Cu₃Si-phase and its modulations during our experiments. For the phase and structural measurements, we recorded high resolution (HRTEM) images and selected area electron diffraction (SAED) patterns, under Jeol3010 and Philips CM20 transmission electron microscopes, respectively. By analyzing SAED patterns and HR images, we found that the η -phase's stuructural model doesn't fit our experimental data and that many modulations of the phase formed under the experimental conditions.

Through measurements, calculations and modelling we gave a new structural model for the η -Cu₃Si-phase (Table 1.) and solved two of the many modulations formed by the different ordering of the Cu – Si atoms forming supercells. One modulations HRTEM image is shown in Figure 1. with its simulated counterpart. During the heating experiment not all the amorphous silicon reacted with the copper, hence all of our experimental data are combination of signals from the reaction products between the copper grid and the 10 nm thick a-Si layer and the unreacted amorphous silicon layer (a-Si) underneath. It is known that overlapping an amorphous layer reduces aesthetic quality of both HRTEM images (see Fig.1) and SAED patterns, however structural data can still be retrieved from these.

| # | Occupancy | X | У | Z |
|---|-----------|--------|--------|--------|
| 1 | Cu 1.000 | 0.0000 | 0.0000 | 0.0000 |
| 2 | Cu 0.500 | 0.6667 | 0.3333 | 0.1667 |
| 3 | Si 1.000 | 0.3333 | 0.6667 | 0.1667 |

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| 2 | |
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| 4 | Cu 1.000 | 0.0000 | 0.0000 | 0.3333 |
|---|----------|--------|--------|--------|
| 5 | Cu 1.000 | 0.6667 | 0.3333 | 0.5000 |
| 6 | Cu 1.000 | 0.3333 | 0.6667 | 0.5000 |
| 7 | Cu 1.000 | 0.0000 | 0.0000 | 0.6667 |
| 8 | Si 1.000 | 0.6667 | 0.3333 | 0.8333 |
| 9 | Cu 0.500 | 0.3333 | 0.6667 | 0.8333 |
| 9 | Cu 0.500 | 0.3333 | 0.6667 | 0.8333 |

Table II: Occupancies and atomic coordinates for the modified Cu₃Si structure; space group: P-3m1, a_0 : 4.06 Å, c_0 : 7.33 Å.



Figure 1 Raw [100] projected experimental HRTEM image of modulated Cu₃Si with four times of the (100) periodicity (= 14.0 Å) of the basic structure (a), its Fourier-transform (b) and the Fourier-filtered experimental image (c)

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