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An accurate determination of the surface energy of solid selenium

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Selenium is currently a key element for developing nano and micro-technologies. Nevertheless, the surface energy of solid selenium (γ_{Se}) reported in the literature is still questionable. In this work, we have measured $\gamma_{Se} = 0.291 \pm 0.025 \text{ J/m}^2$ at 293 K using the sessile drop technique with different probe liquids, namely ethylene glycol, de-ionized water, mercury, and gallium. This value is in excellent agreement with theoretical predictions. © 2012 American Institute of Physics.

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Recently, selenium has been identified as an energy-critical element.^{1,2} This means that it will be vital for the development of technologies such as solar cells. It is defined as a chemical element that is required for emerging sustainable energy sources and that might encounter supply disruptions. Currently, selenium is an important component in thin-film photovoltaic panels^{3,4} and in quantum dots sensitized solar cells.⁵ For optical applications, it is also used in light emitting diodes as CdSe quantum dots.⁶ Selenium is also used in computer memories as component of phase change materials developed in nano/micro-electronics.⁷ In most of these applications, the material surface plays a critical role. Therefore, the surface properties of selenium, and more particularly its solid surface energy (γ_{Se}), has to be carefully determined.

Historically, a lower limit value of γ_{Se} was determined around $\sim 0.175 \text{ J/m}^2$ in 1971, by extrapolating the surface energy of the melt of selenium at 20 °C. An attempt to determine γ_{Se} , by using contact angle measurements involving various liquids presenting a surface energy ranging from 0.028 J/m^2 to 0.052 J/m^2 , failed to be more precise than the extrapolated value due to the adsorption of water or other contaminants on the selenium surface.⁸ Recently, a study dedicated to the size effect on the thermal expansion coefficient of Se (α_{Se}) revealed a significant discrepancy between the theoretical and experimental values.⁹ Since the theoretical evaluation of α_{Se} includes γ_{Se} as an input (0.175 J/m^2), the correctness of the reported value has been questioned since the theory⁹ works well for other materials and properties.^{9–11} Size dependency of the surface energy has to be considered for particle sizes below $\sim 4 \text{ nm}$; however, in our case, it has been ignored due to the fact that we analyzed the thermal expansion coefficient of nanoparticles with sizes higher than 10 nm, therefore, well above the limit of 4 nm. This is justified by the fact that the size effect on surface energies is less than 4% for sizes higher than 4 nm.^{12,13} Therefore, by fitting the experimentally determined values of α_{Se} , γ_{Se} has been theoretically predicted to be around $0.285 \pm 0.022 \text{ J/m}^2$.

The objective of this paper is to experimentally determine γ_{Se} using different probe liquids in order to support the theoretical findings from Ref. 9.

An accepted common procedure to measure a surface energy is through measuring the contact angle with a goniometer via the utilization of the Young's equation, which links the contact angle with the solid surface energy:^{14,15}

$$\gamma_{lv} \cos \theta + \gamma_{sl} = \gamma_{sv}, \quad (1)$$

where γ_{lv} is the liquid-vapour surface energy (also called surface tension), γ_{sl} is the interfacial surface energy, γ_{sv} is the solid-vapour surface energy (γ_{Se} in this work), and θ is the contact angle—defined as the angle between the liquid-solid interface and the liquid-vapour interface. One should note that the surface energy is defined as the excess free energy per unit area of a particular interface¹⁶—i.e., this is the energy required to create surface. Knowing the liquid surface energy of different probe liquids and measuring θ , the difference $\gamma_{sv} - \gamma_{sl}$ can be evaluated. One can easily compute the surface energy of the solid if the differential in Eq. (2) equals zero.

$$d(\gamma_{sv} - \gamma_{sl})/d\gamma_{lv} = 0. \quad (2)$$

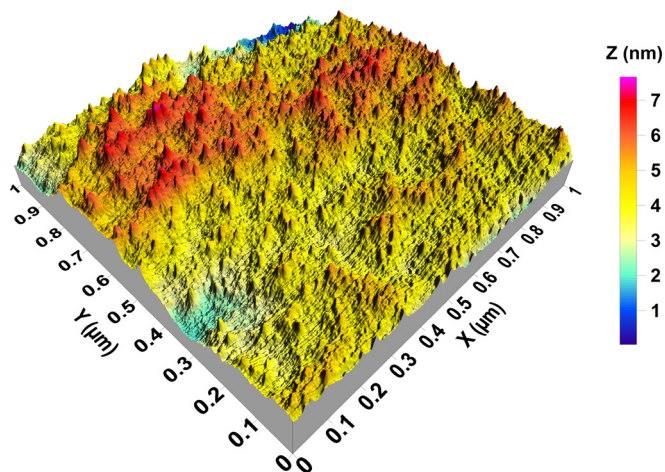


FIG. 1. AFM image ($1 \mu\text{m} \times 1 \mu\text{m}$) of the selenium film.

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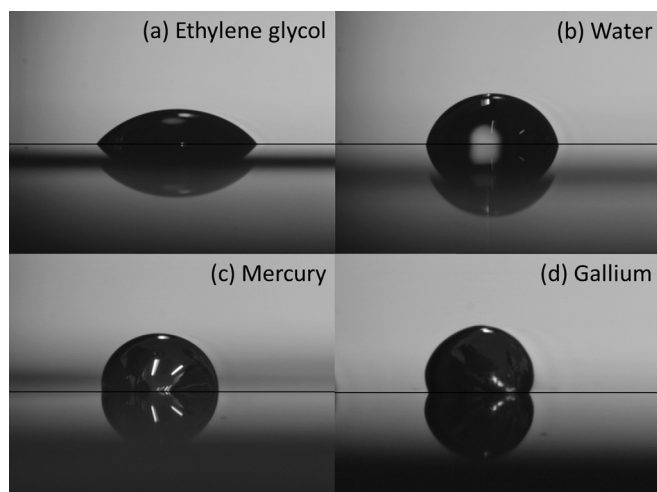


FIG. 2. Photographs illustrating the contact angle obtained for different probe liquids: (a) ethylene glycol, (b) de-ionized water, (c) mercury, and (d) gallium deposited onto the selenium surface. The photographs are side view images where the thin black line indicates the profile of the contact surface between the probe liquid and the selenium. These contact angle measurements were carried out using the sessile drop method.

Indeed, when $\gamma_{lv} \cos \theta$ is maximum and positive, the difference between γ_{sv} and γ_{sl} is also maximum and positive meaning that $d\gamma_{sl}/d\gamma_{lv} = 0$ when $\gamma_{lv} = \gamma_{sv}$.

Experimentally, a 190 nm thick Se thin film was prepared by thermal evaporation of high purity selenium ($\geq 99.999\%$, Sigma-Aldrich) on a $\langle 100 \rangle$ silicon substrate in a vacuum chamber (pressure $\sim 10^{-6}$ mbar). The selenium surface has been characterized by atomic force microscopy (Dimension D3100, Bruker-Veeco, USA). The AFM image (Figure 1) has been processed with the wSX software¹⁷ and the RMS roughness value has been determined to be ~ 1.04 nm. The crystallographic orientation of the film has been determined by X-ray diffraction. The selenium is preferentially oriented along the $\langle 101 \rangle$ direction.

In this work, θ has been evaluated in a class ISO 5/7 cleanroom ($T = 20^\circ\text{C} \pm 0.5^\circ\text{C}$; $RH = 45\% \pm 2\%$). To avoid any contamination, the Se surface was cleaned using VLSI

TABLE I. Liquid surface energy of each probe liquid and mean contact angle obtained on the selenium thin film for each probe liquid.

Liquid	γ_{lv} (J/m ²) ²⁴	θ_{mean} (°)
Ethylene glycol	0.047	47.2 ± 1.9
De-ionized water	0.072	74.4 ± 1.8
Mercury	0.476	83.6 ± 4.2
Gallium	0.718	102.2 ± 5.5

grade solvents, then rinsed with de-ionized water and finally dried with nitrogen gas. After this cleaning procedure, a droplet of probe liquid was deposited by the sessile drop technique onto the film and a high resolution camera captured the image (Figure 2). The diameter of each droplet was less than its capillary length to ensure that the effects of gravity can be ignored. The selected probe liquids should be liquid below the bulk melting temperature of selenium (217°C), and should have liquid surface energy higher than the expected γ_{Se} (0.285 J/m^2). Thus, mercury and gallium, which are liquid at room temperature and at 30°C , respectively, and which have a liquid surface energy around 0.476 and 0.718 J/m^2 , respectively, were selected. Gallium was heated to 40°C prior to deposition onto the Se surface—which was also heated to 40°C . To complete the study, de-ionized water and ethylene glycol, two common liquids used in surface energy determination, were also selected (Table I). Therefore, the wide range of liquid surface energies (0.047 – 0.718 J/m^2) used in this study encompasses γ_{Se} . For each probe liquid, five drops were deposited onto the Se surface and the contact angle was measured for each drop. The contact angle data were gathered using a commercial contact angle meter (GBX Scientific Instruments, France)— θ values were extracted using an interpolation model.¹⁸ The mean contact angle value (θ_{mean}) is reported in Table I and the droplet profile is illustrated for each system in Figure 2.

The $\gamma_{lv} \cos \theta$ vs γ_{lv} data plotted in Figure 3 can be fitted by using a parabolic fit, which is justified by two different evolutions of θ with the surface energy of the probe liquid

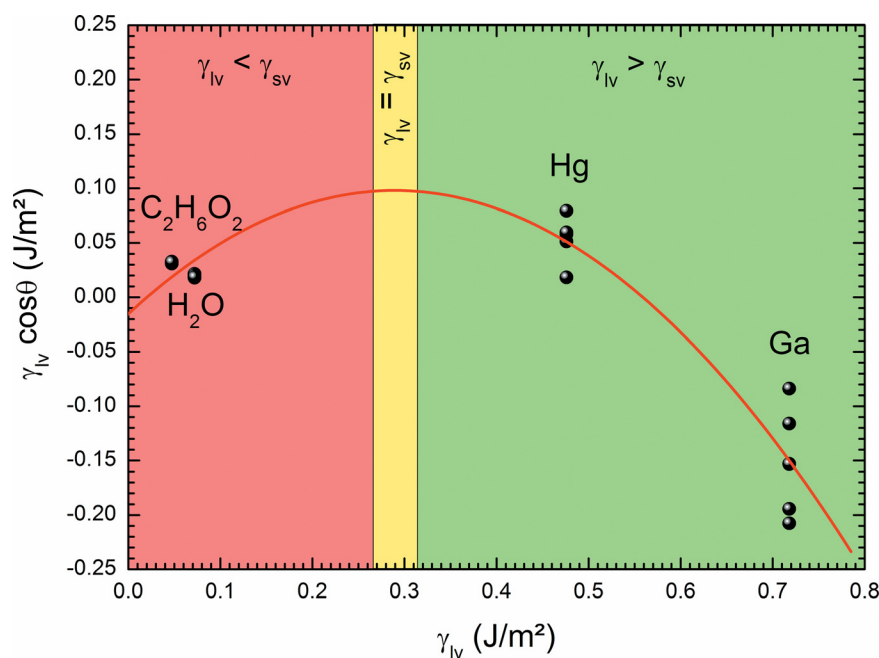


FIG. 3. $\gamma_{lv} \cos \theta$ versus γ_{lv} for a selenium thin film. The red line indicates the evolution of the contact angle with the liquid surface energy of the probe liquid. Three zones are represented: $\gamma_{lv} < \gamma_{sv}$, $\gamma_{lv} = \gamma_{sv}$, and $\gamma_{lv} > \gamma_{sv}$. The zone where $\gamma_{lv} = \gamma_{sv}$ indicates the possible values for the solid surface energy of selenium.

according that the probe liquid has a surface energy lower or higher than γ_{Se} .¹⁹ Indeed, the product $\gamma_{lv} \cos \theta$ increases with γ_{lv} for $\gamma_{lv} < \gamma_{sv}$ —whilst the product $\gamma_{lv} \cos \theta$ decreases with γ_{lv} for $\gamma_{lv} > \gamma_{sv}$. From Eq. (2), it can be deduced that the abscissa value of the maximum of the parabolic fit gives access to γ_{Se} . From our data, $\gamma_{Se} = 0.291 \pm 0.025 \text{ J/m}^2$ has been measured. This value is in excellent agreement with the theoretical value, $\gamma_{Se} = 0.285 \pm 0.022 \text{ J/m}^2$ announced in Ref. 9.

In conclusion, we have precisely determined γ_{Se} using a sessile droplet technique involving various probe liquids in a controlled environment. Generally, probe liquids have a liquid surface energy lower than 0.1 J/m^2 ; therefore, the originality of this paper is to use less conventional probe liquids like mercury and gallium to encompass the solid surface energy of selenium. We have measured $\gamma_{Se} = 0.291 \pm 0.025 \text{ J/m}^2$ which is in excellent agreement with the theoretical value deduced from Refs. 9 and 10. As selenium is a key element for nano and micro-technologies—e.g., solar cells,^{2,20} phase change memories,^{7,21} and antibacterial coatings^{22,23}—the observations described here will be of interest to many communities.

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