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Young’s modulus of Sb\textsubscript{2}O\textsubscript{3} micro- and nanowires determined accurately by a nanomanipulation-assisted thermal resonance method

Antimony trioxide (Sb\textsubscript{2}O\textsubscript{3}) micro- and nanomaterials have been widely used as a fire retardant, and are promising for fabricating high-performance cool materials and optoelectronic devices, but little is known on their mechanical properties. In this study, Young’s moduli of Sb\textsubscript{2}O\textsubscript{3} micro- and nanowires grown via chemical vapor deposition are accurately determined by a nanomanipulation-assisted thermal resonance method. The Sb\textsubscript{2}O\textsubscript{3} micro- and nanowires grow along the [001] direction and have irregular cross sections with thicknesses ranged from 87 to 238 nm and widths ranged from 168 to 549 nm. The measured Young modulus value is 92 ± 7 GPa, which is thickness independent and very close to the value of 89 GPa predicted using the first-principle calculations. The developed method can be extended for accurately measuring the Young’s modulus of any micro- and nanowire with irregular cross section.
the accurate characterization and understanding of the mechanical properties of nanoscale samples remains a significant challenge, due to the uncertainties or limitations of the specific characterization methods used in practical tests. For example, determining the cross-sectional profile of a testing micro- or nanowire is a fundamental requirement for the accurate measurement, but is very hard to achieve for most current methods. Although most nanowires do not have regular cross-sections, they are usually supposed to be a circle, square, regular pentagon, or regular hexagon in current tests. This has been a major error source for most studies.

In our previous studies, we established a resonance method based on the laser Doppler technique for testing the elastic modulus of nanowires. As a noncontact and nondestructive method, this new method can test the elastic modulus of the same nanowire for many times using different resonating lengths, and also accurately determine the temperature dependence of elastic modulus of the same nanowire. In this study, we further developed a nanomanipulation-assisted resonance method that can accurately measure the Young’s moduli of Sb$_2$O$_3$ micro- and nanowires with arbitrary irregular cross sections. In this method, the cross-sectional profiles of the testing micro- and nanowires can be accurately determined by high resolution scanning electron microscopy (SEM).

Sb$_2$O$_3$ nanowires used in this study were synthesized in a horizontal tube furnace by use of catalyst-free chemical vapor deposition. Fig. 1(a) presents a SEM (JEOL JSM-7800F, operated at 5 kV) image of the nanowires collected. From the X-ray diffraction (XRD, Rigaku D max 2500 VB) spectrum shown in Fig. 1(b), it is seen that all diffraction peaks of the sample match well with those of the orthorhombic Sb$_2$O$_3$ (JCPDS Card No. 11-0689; cell constant: a = 0.4911 nm, b = 1.2464 nm, c = 0.5412 nm). Fig. 1(c) shows a low-magnitude transmission electron microscopy (TEM, FEI Tecnai F20 operated at 200 kV) image of a nanowire with a uniform lateral size along the axial direction. From the high-resolution TEM image of the nanowire shown as Fig. 1(d), the lattice spacings are measured to be 0.49 and 0.27 nm, which correspond to the (100) and (002) planes of orthorhombic Sb$_2$O$_3$, respectively. The corresponding selected area electron diffraction (SAED) analysis further confirmed the nanowire has a single crystal structure grown along the [001] direction. Energy dispersive X-ray spectroscopy (EDS, attached to FEI Tecnai F20) analysis in Fig. 1(e) also confirmed that the nanowire is composed of Sb and O with an atomic ratio close to 2:3.

The nanomanipulation-assisted resonance measurement was performed as follows. A nanowire was firstly transferred to the edge of a smooth Si substrate to form a nanowire cantilever with the aid of optical microscope based nanomanipulation. Here, the nanowire cantilever was clamped by the van der Waals adhesion between the nanowire and substrate, and also accurately determine the temperature dependence of elastic modulus of the same nanowire. In this method, the cross-sectional profiles of the testing micro- and nanowires can be accurately determined by high resolution scanning electron microscopy (SEM).

According to the Euler–Bernoulli beam theory, the Young’s modulus, $E$, of an ideally clamped nanowire with a uniform cross-section can be derived by Refs. 29 and 33,

$$E = \frac{4\rho A\pi^2 f_n^2}{\beta_n^4 I}, \quad n = 1, 2, 3, \ldots$$

FIG. 1. (a) SEM image and (b) XRD diffractogram of the as-synthesized micro- and nanowires. (c) Low-magnification TEM image, (d) High-resolution TEM image, and (e) EDS pattern of a typical Sb$_2$O$_3$ nanowire. The insects in (d) shows the corresponding SAED pattern.
where $f_n$ are the natural frequencies, $L$ is the resonating (suspending) length, $I$ is the area moment of inertia, $A$ is the cross-sectional area, $\rho (= 5.67 \text{ g/cm}^3)$ is the density of orthorhombic $\text{Sb}_2\text{O}_3$ nanowires, while $\beta_n (= 1.875, 4.694, 7.855, \ldots$ for $n = 1, 2, 3, \ldots$) are the constants satisfying the transcendental equation, $\cos \beta_n \cosh \beta_n + 1 = 0$. As a result, for an ideal nanowire cantilever, we have,\(^{29,30}\)

$$f_1: f_2: f_3: \ldots = 1: 6.27: 17.55: \ldots \quad (2)$$

If the nanowire is not well clamped onto the substrate or its cross-section along the resonating length is not uniform, the measured frequency ratios will deviate from the values defined by Eq. (2), which will thus underestimate or overestimate the modulus value.\(^{34–36}\) As a result, Eq. (2) can be used as a criterion to evaluate whether the measurement is reliable and accurate.

Fig. 3(a) presents a low-magnification SEM image of a $\text{Sb}_2\text{O}_3$ nanowire clamped at the edge of a Si substrate by the nanowire-substrate adhesion. The nanowire cantilever has a uniform lateral size along the whole suspending length of $20.94 \pm 0.05 \mu\text{m}$ and a width of $347 \pm 3 \text{nm}$. Fig. 2(b) is the high-magnification SEM image of the corresponding cross-sectional profile of the nanowire cantilever, which was manipulated back onto the substrate edge. Clearly, the width of nanowire is the same as that obtained from Fig. 3(a), while the thickness is $146 \pm 3 \text{nm}$. The cross-sectional profile of the nanowire could be digitized using Matlab as shown in Fig. 3(c), and the corresponding cross-sectional area and the area moment of inertia could be accurately determined to be, $A = (4.4 \pm 0.1) \times 10^{-14} \text{ m}^2$ and $I = (6.7 \pm 0.5) \times 10^{-29} \text{ m}^4$, respectively. Fig. 3(d) displays the thermal vibration spectra of the nanowire cantilever collected by the scanning laser Doppler vibrometer. The first two natural frequencies, $f_1$ and $f_2$, are $204.4 \pm 0.4$ and $1277.2 \pm 0.4 \text{ kHz}$, respectively. The ratio, $f_1:f_2 = 1:6.25$, agrees excellently with the theoretical value defined by Eq. (2). This undoubtedly confirms that the nanowire cantilever is uniform along the axial direction and well clamped by the van der Waals adhesion at the nanowire-substrate interface. Substituting the values of $L, A, I, f_1$ and $f_2$ into Eq. (1), we obtain $E_1 = 94.8 \pm 4.8 \text{ GPa}$ and $E_2 = 94.2 \pm 4.8 \text{ GPa}$, where the error values come from the uncertainties in the length, cross-section size, and natural frequencies. On the other hand, if the cross-section could not be directly determined by SEM, we have to assume it is a circle or

![Diagram](image_url)
regular hexagon with a diameter, \( d = 347 \) nm. For the case of circular cross-section, substituting \( A_C = \pi d^2/4 \) and \( I_C = \pi d^4/64 \) into Eq. (1), we obtain \( E_C = 19.2 \) GPa. For regular hexagonal cross-section, using \( A_H = 3\sqrt{3}d^2/8 \) and \( I_H = 5\sqrt{3}d^4/256 \), we have \( E_H = 23.0 \) GPa. Obviously, these estimated values are significantly lower than the corresponding value derived from the accurate cross-sectional profile obtained by SEM.

In our test we measured 9 \( \text{Sb}_2\text{O}_3 \) micro- and nanowire cantilevers. The \( f_2/f_1 \) values for these cantilevers fell in the range of 6.10 to 6.41, very close to the theoretical value of 6.27 defined by Eq. (2). This suggests that the measured micro- and nanowires should be uniform along the axial direction and reliably clamped by van der Waals adhesion. Detailed SEM analyses revealed that the cross-section profiles of these micro- and nanowires are somehow irregular, as shown in Fig. 4(a–h). Unlike the thin \( \text{ZnO} \) nanowires, \(^{20,22} \) the thickness-independent elastic modulus of our \( \text{Sb}_2\text{O}_3 \) micro- and nanowires should be mainly related to their relatively great thickness. In addition, unlike \( \text{ZnO} \), \( \text{Sb}_2\text{O}_3 \) does not have obvious stiffening effects from surface relaxation as predicted in the theoretical simulations. \(^3 \) For comparison, we also plotted the estimated Young’s modulus values for the 9 samples in Fig. 4(i), assuming they have circular or regular hexagonal cross sections. It is found that the values scattered in the range of 5 - 70 GPa with an average value of 24 GPa, and 5 - 84 GPa with an average value of 27 GPa, for circular and hexagonal cross sections, respectively. These values are quite similar to the range of 16 - 48 GPa with an average value of 34 GPa for [001]-oriented \( \text{Sb}_2\text{O}_3 \) micro- and nanorods, estimated using square or rectangular cross sections. \(^7 \) Obviously, the consistency depends heavily on the accurate determination of cross sections, while the suppositions of circular, square or hexagonal cross-sections will lead to significantly scattering results. To validate our experimental results, we further derived out the intrinsic Young’s modulus value for orthorhombic \( \text{Sb}_2\text{O}_3 \) along [001] direction by Ref. 37,

\[
E_{001} = \frac{2c_{13}}{c_{11} + c_{12}},
\]

where \( c_{11} = 234.2 \) GPa, \( c_{12} = 100.2 \) GPa, \( c_{13} = 103.2 \) GPa, and \( c_{33} = 153.0 \) GPa are the theoretical elastic constants predicted recently by first-principle calculations. \(^{37} \) Substituting the values of \( c_{11}, c_{12}, c_{13}, \) and \( c_{33} \) into Eq. (3), we obtained \( E_{001} = 89 \) GPa, which matches well our experimental value of 92 ± 7 GPa.

In summary, we synthesized [001]-oriented \( \text{Sb}_2\text{O}_3 \) micro- and nanowires with irregular cross-sections using chemical vapor deposition, and characterized the Young’s moduli of the as-synthesized micro- and nanowires with thicknesses ranged from tens to several hundred nm and widths of several hundred nanometers by use of the nanomanipulation-assisted resonance method. The measured average values of 92 GPa are size-independent, and agree well with the theoretical intrinsic value of ~ 89 GPa obtained by the first-principle calculations. Our test provides a reliable and fundamental mechanical parameter for \( \text{Sb}_2\text{O}_3 \), which will be valuable for the design and operation of \( \text{Sb}_2\text{O}_3 \) based devices or composites.
The nanomanipulation-assisted resonance method developed here can effectively remove the uncertainties in determining the clamping conditions and cross-sectional profiles of the testing samples, and is expected to a universal method for accurately measuring the elastic modulus of nanowires with arbitrary irregular cross sections.

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REFERENCES

1. S. Zhang and A. R. Horrocks, Prog. Polym. Sci. 28(11), 1517–1538 (2003).
2. G. Venkateshwarlu, K. C. Rajanna, and P. K. Saiprakash, Synth. Commun. 39(3), 426–432 (2009).
3. Y. Qi, S. Zhu, and J. Zhang, Energy and Buildings 172, 47–56 (2018).
4. S. S. Kim, H. G. Na, Y. J. Kwon, H. Y. Cho, and H. W. Kim, Metals and Materials International 21(2), 415–421 (2015).
5. Z. T. Deng, D. Chen, F. Q. Tang, J. Ren, and A. J. Muscat, Nano Research 2(2), 151–160 (2009).
6. Y. Wang, L. Jiang, Y. Liu, D. Tang, F. Liu, and Y. Lai, J. Alloys Compd. 727, 469–474 (2017).
7. H. Lun, J. Ouyang, A. Tang, and H. Yang, Nano 10(6), 1550078 (2015).
8. M. Deng, S. Li, W. Hong, Y. Jiang, W. Xu, H. Shuai, G. Zou, Y. Hu, H. Hou, W. Wang, and X. Ji, Mater. Chem. Phys. 223, 46–52 (2019).
9. Y. Wang, L. Jiang, Y. Liu, D. Tang, F. Liu, and Y. Lai, J. Alloys Compd. 727, 469–474 (2017).
10. H. Lun, J. Ouyang, A. Tang, and H. Yang, Nano 10(6), 1550078 (2015).
11. J. Li, Z. W. Shan, and E. Ma, MRS Bulletin 39(2), 108–117 (2014).
12. L. H. Wang, Z. Zhang, and X. D. Han, NPG Asia Materials 5, e40 (2013).
13. D. Mordahat, O. David, and R. Kostitski, Adv. Mater. 30(41), 1706710 (2018).
14. S. Wang, Y. He, H. Huang, J. Zou, J. G. Auchterlonie, L. Hou, and B. Huang, Nanotechnology, 24(28), 285703 (2013).
15. S. Wang, Y. Wu, L. Lin, Y. He, and H. Huang, Small 11(14), 1672–1676 (2015).
16. E. W. Wong, P. E. Sheehan, and C. M. Lieber, Science 277(5334), 1971–1975 (1997).
17. S. Vlassov, B. Polyakov, L. M. Dorogin, M. Antsov, M. Uralas, R. Saar, R. Löhmus, and I. Kink, Mater. Chem. Phys. 143(3), 1026–1031 (2014).
18. M.-F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, and R. S. Ruoff, Science 287(5453), 637–640 (2000).
19. E. Xu, Q. Qin, A. Mishra, Y. Gu, and Y. Zhu, Nano Research 3(4), 271–280 (2010).
20. R. Agrawal, B. Peng, E. E. Gdoutos, and H. D. Espinosa, Nano Lett. 8(11), 3668–3674 (2008).
21. M. M. J. Treacy, T. W. Ebbestos, and J. M. Gibson, Nature 381(6584), 678–680 (1996).
22. C. Q. Chen, Y. Shi, Y. S. Zhang, J. Zhu, and Y. J. Yan, Phys. Rev. Lett. 96(7), 075505 (2006).
23. S. Wang, Z. Shan, and H. Huang, Adv. Sci. 4(4), 1600332 (2017).
24. Y. Chen, X. An, and X. Liao, Applied Physics Reviews 4(3), 031104 (2017).
25. Y. Zhu, Applied Mechanics Reviews 69(1), 010402 (2017).
26. S. Zimmermann, W. Klauser, J. Mead, S. Wang, H. Huang, and S. Fatikow, Nano Research 12(2), 389–396 (2019).
27. J. L. Mead, H. Xie, S. Wang, and H. Huang, Nanoscale 10, 3410–3420 (2018).
28. T.-H. Chang, G. Cheng, C. Li, and Y. Zhu, Extreme Mechanics Letters 8, 177–183 (2016).
29. S. Wang, G. Chen, H. Huang, S. Ma, H. Xu, Y. He, and J. Zou, Nanotechnology 24(30), 305705 (2013).
30. S. Wang, Q. Huang, Y. Wu, and H. Huang, Nanotechnology 27(47), 475701 (2016).
31. A. Roy, S.-p. Ju, S. Wang, and H. Huang, Nanotechnology 30(6), 065705 (2019).
32. A. Roy, J. Mead, S. Wang, and H. Huang, Scientific Reports 7(1), 9547 (2017).
33. R. D. Blevins, Formulas for natural frequency and mode shape (Van Nostrand Reinhold, New York, 1979).
34. R. S. Ruoff, X. Q. Chen, S. L. Zhang, G. J. Wagner, and W. Q. Ding, J. Appl. Phys. 95(9), 4823–4828 (2004).
35. D. J. Zeng and Q. S. Zheng, Phys. Rev. B 76(7), 075417 (2007).
36. W. Shi, J. Zou, K. Y. Lee, and X. F. Li, Mod. Phys. Lett. B 32(7), 1850095 (2018).
37. L. A. Shuvalov, in Modern Crystallography IV, edited by L. A. Shuvalov (Springer-Verlag Berlin Heidelberg, 1988), Vol. 37, pp. 50-177.