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Properties of SbSI@CNTs and SbSI nanowires

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³ Department of Physics, Wright State University, Dayton, Ohio, USA.
Subjects presented\textsuperscript{1} at DSL-2011:

- sonochemical preparation of \textit{antimony sulfoiodide} (SbSI)-type nanowires,

- sonochemical filling of carbon nanotubes with SbSI (SbSI @ CNTs),

- ultrasonic welding of CNTs to metal electrodes.

\textsuperscript{1} M. Nowak, K. Koziol, G. Kozlowski, J. Berdowski, J. Kasperczyk, I. Kityk, K. Mistewicz, M. Jesionek, \textit{Ultrasonics and Carbon Nanotubes}, Special Session: Carbon and Oxide Based Nanostructured Materials at the 7\textsuperscript{th} Internat. Conf. DSL-2011, Algarve, Portugal.
Properties of SbSI

- semiconductor \((E_{glf} = 1.83(3) \text{ eV})\)
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- low coercive field ( $E_c=10^4$ V/m (T=0°C, 50 Hz) )
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- ferroelectric ($T_c = 292(1)$ K)
- high spontaneous polarization ($P_s = 0.30$ C/m$^2$)
- low coercive field $E_c = 10^4$ V/m ($T=0^\circ$C, 50 Hz)
- high electromechanical coupling ($k_{33} = 0.9$)
Properties of SbSI

- high piezoelectric modulus \( d_{333} = 7(2 \cdot 10^{-9} \text{ m/V}) \)
Properties of SbSI

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Properties of SbSI

- high piezoelectric modulus \( (d_{333} = 7(2 \cdot 10^{-9} \text{ m/V}) \)

- strong electrostriction \( (Q_{3333} = 1.3 \cdot 10^{-13} \text{ m}^2/\text{V}^2) \)

- very high pyro-optical coefficient along c axis
  \( (\cdot 10^{-3} \text{ K}^{-1}) \)
Properties of SbSl

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- pyroelectric \( (60 \text{ mC}/(\text{m}^2\text{K})) \)
Properties of SbSI

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- pyroelectric (60 mC/(m\(^2\)K)

- strong anisotropy
- strong anisotropy

$a = 0.853 \, \text{nm}$, $b = 1.017 \, \text{nm}$, $c = 0.408 \, \text{nm}$
Comparison of filtered HRTEM image of SbSI nanowires (A) with calculated distribution of atoms (B - view comparable with the experiment; C - view along the c axis of the SbSI nanowires; • Sb, ○ S and ● I atoms; line shows the (210) plane; red rectangle presents cell in SbSI crystal).
- strong anisotropy

\[ a = 0.853 \text{ nm}, \quad b = 1.017 \text{ nm}, \]
\[ c = 0.408 \text{ nm} \]
SbSI @ CNTs
SbSeI @ CNTs
Befor and after sonochemical synthesis of SbSI in ethanol

The sonochemical technique based on cavitation is:

- convenient,
- fast,
- efficient technique of nanotechnology.
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Befor and after sonochemical synthesis of SbSI in ethanol

\[ S = 0.486g \]
\[ Sb = 1.847g \]
\[ I = 1.928g \]
Image (a) and typical SEM micrograph (b) of sonochemically prepared SbSi gel.
HRTEM image of individual nanowire of SbSI
Dried multiwalled CNTs filled with SbSI sonochemically in methanol.

Typical SEM micrograph of dried multiwalled CNTs filled with SbSI sonochemically in methanol.
Dried multiwalled CNTs filled with SbSI sonochemically in methanol.

Typical SEM micrograph of dried multiwalled CNTs filled with SbSI sonochemically in methanol.

TEM line scan EDS for SbSeI encapsulated in CNT
New subject:

sensing properties of SbSI @ CNTs and SbSI nanowires
Electrical investigations of no welded SbSI@CNTs or SbSI nanowires

1- electrodes,
2- SbSI@CNTs or SbSI nanowire,
3- CNT or surface layer,
4- SbSI nanowire.
Influence of temperature and humidity on Nyquist plots of SbSI gel

- $T = 289$ K, RH = 87 %;
- $T = 291$ K, RH = 86 %;
- $T = 293$ K, RH = 85 %;
- $T = 295$ K, RH = 84 %;
- $T = 297$ K, RH = 84 %;
- $T = 299$ K, RH = 83 %;
- $T = 300$ K, RH = 80 %;
- $T = 302$ K, RH = 57 %;
- $T = 304$ K, RH = 45 %;
- $T = 306$ K, RH = 41 %;
- $T = 308$ K, RH = 36 %;
- $T = 310$ K, RH = 34 %;
E = 290 V/m, $p = 1$ atm).
Influence of temperature and humidity on Nyquist plots of SbSI gel:

- T = 289 K, RH = 87 %
- T = 291 K, RH = 86 %
- T = 293 K, RH = 85 %
- T = 295 K, RH = 84 %
- T = 297 K, RH = 84 %
- T = 299 K, RH = 83 %
- T = 300 K, RH = 80 %
- T = 302 K, RH = 57 %
- T = 304 K, RH = 45 %
- T = 306 K, RH = 41 %
- T = 308 K, RH = 36 %
- T = 310 K, RH = 34 %

E = 290 V/m, p = 1 atm.

Impedance spectroscopy
Influence of temperature on Nyquist plot for SbSI gel for constant humidity (■ – T=281 K; □ – T=304 K; ● – T=281 K; ○ – T=300 K).
Influence of temperature on Nyquist plot for SbSI gel for constant humidity (T=281 K; T=304 K; T=281 K; T=300 K).

RH=80 %

RH=20 %

Sum of the least squares obtained when data registered under different ambient conditions of SbSI gel (black bars) were fitted with different models for

\[ \chi^2 \]

\[ T, \text{ K} \]

\[ \text{RH, \%} \]

\[ 280 \quad 290 \quad 300 \quad 310 \]

\[ 0.000 \quad 0.005 \quad 0.010 \quad 0.015 \quad 0.020 \quad 0.025 \]

\[ 0 \quad 20 \quad 40 \quad 60 \quad 80 \quad 100 \]

\[ \text{RH=39\%} \]

\[ \text{for} \]

\[ \text{for} \]
Influence of temperature on resistance and capacitance parameters of equivalent circuits used to interpret Nyquist plots for different humidities:

- RH = 10 %;
- RH = 20 %;
- RH = 30 %;
- RH = 40 %;
- RH = 55 %

Open signs model:

Full signs model:
Influence of humidity on resistance and capacitance parameters of equivalent circuits used to interpret Nyquist plots for different temperatures:
- RH = 10 %
- RH = 20 %
- RH = 30 %
- RH = 40 %
- RH = 55 %

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- RH = 10 %
- RH = 20 %
- RH = 30 %
- RH = 40 %
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full signs model:
Influence of temperature on frequency response of real (a) and imaginary (b) parts of impedance of SbSI gel for constant humidity:

- T=281 K; RH=20 %
- T=294 K; RH=20 %
- T=304 K; RH=20 %
- T=307 K; RH=20 %
- T=319 K; RH=20 %

\[ 2\pi f_{\text{MAX}} \tau_Z = \frac{1}{31} \]
Influence of temperature on frequency response of real (a) and imaginary (b) parts of impedance of SbSI gel for constant humidity:
- T=281 K; RH=20 %
- T=294 K; RH=20 %
- T=304 K; RH=20 %
- T=307 K; RH=20 %
- T=319 K; RH=20 %

Influence of temperature and humidity on relaxation time of SbSI gel

\[ \tau_z = \tau_{z0} \exp \left( \frac{E_a}{k_B T} \right) \]

\[ E_a = (0.832 \pm 0.067) \text{ eV} \]
\[ \tau_z = \tau_{z0} \exp\left(\frac{E_a}{k_B T}\right) \]

Influence of humidity on pre-exponential factor describing temperature dependence of relaxation time of SbSI gel

\[ \tau_{z0}(RH) = \tau_{z0}(RH = 0) \exp\left(\frac{-RH}{B}\right) + \tau_{ZRH_{\text{max}}} \]

\[ t_{z0}(RH=0) = (2.49 \pm 0.2) \cdot 10^{-16} \text{ s}, \quad B = 5.7 \pm 0.2, \quad t_{ZRH_{\text{max}}} = (0.87 \pm 0.3) \cdot 10^{-18} \text{ s} \]
Influence of humidity on pre-exponential factor describing temperature dependence of relaxation time of SbSI gel.

Comparison of the temperature dependences of resistance parameters of equivalent circuits describing Nyquist plots registered in the cases of SbSI@CNT sonochemically prepared in methanol (R1, R2), and SbSI@CNT (R1, R2) and SbSeI@CNT (R1, R2) ultrasonically prepared in ethanol.

Equivalent circuit describing Nyquist plot of SbSI@CNT sonochemically prepared in methanol

Impedance of constant phase element (CPE)

\[ Z_{CPE} = \left[ A(j\omega)^n \right]^{-1} \]

\( n = 1 \) for ideal capacitor and \( n = 0 \) for ideal resistor
Comparison of the temperature dependences of resistance parameters of equivalent circuits describing Nyquist plots registered in the cases of SbSI@CNT sonochemically prepared in methanol (◊ – $R_1$, • – $R_2$), and SbSI@CNT (■ – $R_1$, □ – $R_2$) and SbSeI@CNT (◇ – $R_1$, ▲ – $R_2$) ultrasonically prepared in ethanol.
Comparison of capacitance parameters of equivalent circuits describing Nyquist plots of SbSI@CNT sonochemically prepared in methanol ($n_1, A_1; n_2, A_2$), and SbSI@CNT ($n, A; C$) and SbSeI@CNT ($C_1, C_2$) sonochemically prepared in ethanol.

SbSI after 30 min. of sonochemical synthesis in toluene

SbSI after 120 min. of sonochemical synthesis in toluene
Comparison of capacitance parameters of equivalent circuits describing Nyquist plots of SbSI@CNT sonochemically prepared in methanol (◆ – n₁, A₁; ◊ – n₂, A₂), and SbSI@CNT (■ – n, A; ■ – C) and SbSeI@CNT (□ – C₁; □ – C₂) sonochemically prepared in ethanol.
Comparison of inductance parameters of equivalent circuits describing Nyquist plots of SbSI@CNT sonochemically prepared in methanol (●), and SbSI@CNT (■) and SbSeI@CNT (□) ultrasonically prepared in ethanol. $^{39}$
Comparison of the temperature dependences of relaxation time of SbSI@CNT sonochemically prepared in methanol (♦ - $t_1$, ◊ - $t_2$), and SbSI@CNT (■) and SbSeI@CNT (□) ultrasonically prepared in ethanol.\textsuperscript{40}
Temperature dependence of SbSI @ CNT d.c. resistance

(p = \cdot 10^{-3} \text{ mbar}; \text{ vertical line represents } T_c = 293 \text{ K for bulk crystals})
Temperature dependence of SbSI @ CNT d.c. resistance

$\text{Al}_2\text{O}_3$ single crystal
Ultrasonic nanowelding

1 - ultrasonic generator 70 kHz
   ADG70-100P-230-NO
   (Rinco Ultrasonics)
3 - transducer C 70-2
   (Rinco Ultrasonics)
5 - digital scale

2 - holder
4 - special sonotrode made by myself
   (surface roughness - order of magnitude nm)
6 - sample
Ultrasonic nanowelding

1 - ultrasonic generator 70 kHz
ADG70-100P-230-NO (Rinco Ultrasonics)

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6 - sample

SiC single crystal
Si/SiO$_2$ substrates

made by:
Wroclaw University of Technology;
electrode spacing: 0.6, 1.2 or 2.5 $\mu$m
Alignment in electric field

- SbSI nanowires ultrasonically agitated in toluene \((C_6H_5CH_3)\)
- applied electric field \(E = 5 \text{ V/m}\)
SbSI nanowires on Si/SiO$_2$ substrate with Au electrodes after ultrasonic nanowelding.
Nanowires of SbSI on Si/SiO₂ substrate with Au electrodes after ultrasonic welding
Ultrasonic bonding

The electrical contacts made using wedge ultrasonic bonding.
Carbon nanotubes on Si/SiO₂ substrate with Au electrodes after ultrasonic welding
Glass Substrates

made by: Abtech Scientific Inc.
electrode spacing: 1 μm
Nanowires of SbSI on glass substrate

\[ I, \text{ pA} \]

\[ E, 10^6 \text{V/m} \]

\( T=298 \text{ K} \)

- lean substrate
- after deposition
- after ultrasonic welding
DC electrical measurements

\[ I = (A_0 E + B_0) + C_0 E^2 \quad [14] \]

- ohmic conductivity
- space charge

<table>
<thead>
<tr>
<th>T, K</th>
<th>283.1</th>
<th>297.9</th>
<th>333.7</th>
</tr>
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<tbody>
<tr>
<td>A_0, 10^{-18} S m</td>
<td>0.662(10)</td>
<td>1.901(37)</td>
<td>4.607(14)</td>
</tr>
<tr>
<td>B_0, 10^{-14} A</td>
<td>5.20(91)</td>
<td>5.0(33)</td>
<td>-17.9(13)</td>
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<tr>
<td>C_0, 10^{-25} S m^2/V</td>
<td>1.717(23)</td>
<td>0.365(85)</td>
<td>3.574(33)</td>
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Current-voltage characteristics of SbSI single nanowires at different temperatures:
- T=283.1 K; - T=297.9 K; - T=333.7 K;  \( p=1.3(7)\times10^{-5} \) mbar;
- fitted curves.
Current-voltage characteristics of SbSI single nanowires at different temperatures:
- $T = 283.1\, \text{K}$;
- $T = 297.9\, \text{K}$;
- $T = 333.7\, \text{K}$;
- $p = 1.3(7) \times 10^{-5}\, \text{mbar}$; fitted curves.

$I = (A_0 E + B_0) + C_0 E^2$

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Kinetics of photocurrent in unilluminated (a) and illuminated (b) SbSI nanowire measured for different light intensities:
- - 100% $I_0$,
- - 63% $I_0$,
- - 40% $I_0$,
- - 25% $I_0$,
- - 10% $I_0$ ($\lambda=488\, \text{nm}$, $I_0=2.4 \times 10^{22}\, \text{photon/(m}^2\text{s})$, $E=2.0 \times 10^6\, \text{V/m}$, $T=298\, \text{K}$).
Photoconductivity of SbSI nanowires

Photocurrent as a function of light intensity 
($\lambda$=488 nm, $E$=2.0x10$^6$ V/m, $T$=298 K).
\[ I_{\text{Bc}}(\lambda, T) = A(\lambda, T)I_0\gamma(\lambda, T) \]

![Graph showing photocurrent as a function of light intensity with various temperatures: - 283 K, - 303 K, - 323 K.](image)
A 5 μm thick film of aligned SbSI nanowires on alumina substrate with interdigitated platinum lines as electrodes and the platinum temperature detector (5 V/m).

Low density of aligned SbSI nanowires on Al₂O₃ substrate (5 V/m)
Nanowires of SbSI nanowelded to electrodes on glass substrate
SbSI nanowires nanowelded to electrodes on glass substrate

0.5 ml/min

4 ml/min
SbSI nanowires nanowelded to electrodes on glass substrate

E = \(2.5 \times 10^5\) V/m

1 ml/min

E = \(2.5 \times 10^5\) V/m

5 ml/min
DC electrical measurements

\[ I(t) = I_0 e^{-\frac{t}{\tau}} + I_{dc} \]

<table>
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<th>Parameter</th>
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<tr>
<td>( \tau ) s</td>
<td>10.74(28)</td>
</tr>
<tr>
<td>( I_0 ) mA</td>
<td>2.9(15)</td>
</tr>
<tr>
<td>( I_{dc} ) pA</td>
<td>6.879(16)</td>
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Time dependence of applied electric field (E) and current response (I) measured for SbSI single nanowires (\( p = 1.2 \times 10^{-5} \) mbar, \( T = 298.4 \) K).
Current vs. relative humidity in the case of aligned no welded SbSI nanowires

(\(\lambda=465\) nm; \(I_0=19\) photon/(m\(^2\)s); \(T = 280\) K; \(T = 303\) K)
Kinetics of photocurrent in alligned no welded SbSI nanowires
(λ=465 nm; I₀=19 photon/(m²s); T=303 K)
Kinetics of photocurrent in no welded SbSI xerogel in vacuum
(A- $\lambda$=465 nm; B- $\lambda$=518 nm;
C= $\lambda$=660 nm; $p$=1.1 mbar; $T$=288 K; $I_0$= $\cdot$ 19 photon/(m^2s))

Influence of humidity on kinetics of photocurrent in SbSI xerogel in N_2
($\lambda$=488 nm; $I_0$= $\cdot$ 21 photon/(m^2s))
Influence of temperature on electric current in SbSI xerogel in different environment

A- vacuum, \( p = 1.1 \) mbar;
B- moist \( N_2 \), \( RH = 78 \% \) at \( T = 285 \) K and \( p = 987 \) mbar.
Directions of future investigations

• gas nanosensors constructed from single nanowires of SbSI and SbSI@CNTs

• photodetectors constructed from single nanowires of SbSI and SbSI@CNTs
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Thank you for your attention