Proceedings of the IASTED International Conference
Solar Energy (SOE 2009)
March 16 - 18, 2009 Phuket, Thailand

THERMOELECTRIC PROPERTIES AND NANOSTRUCTURES OF MATERIALS PREPARED FROM RICE HUSK ASH

Supakorn Pukird[1]*, Udom Tipparach[1], Pristanuch Kasian[1] and Pichet Limsuwan[2]
[1]Department of Physics, Faculty of Science, Ubon Ratchathani University,
Ubon Ratchathani, , 34190,Thailand
[2]Department of Physics,Faculty of Science, King Mongkut's University of Technology Thonburi,
Bangkok, 10140,Thailand.
*Corresponding author: psupakor27@yahoo.com

ABSTRACT
We studied the thermo-electrical properties of ceramics prepared from rice hush ash. The materials were made from burning rice husk ash and coconut shell at different temperatures. Several metal oxides were mixed in these materials. The resultant powder was pressed into pellets. The pellets were heated at temperature of 700 °C for 1-3 hours, they resemble ceramics. The thermo-electrical property of the ceramics was conducted. The voltages between both sides of the pellets were observed. The electromotive force was found when different temperatures were applied on both sides of the pellet specimens. The Seebeck coefficient was calculated. The results indicate that these materials may be used as thermoelectric devices. The materials sources and the products on the substrates were investigated by scanning electron microscope (SEM) and energy dispersive X-rays (EDX). The images of SEM and EDX showed nanostructures of materials such as nanowires nanorods and nanoparticles of the products and sources.

KEY WORDS
SiO2, rice husk ash, coconut shell charcoal, Seebeck coefficient, thermoelectric properties, nanostructures

1. Introduction

As an agricultural country, Thailand produces a large number of abundant residues such as rice husk and coconut shells. The number of rice production of world is approximate 400 million metric tons per year. Rice husk is a by-product of rice milling which is about 10 % [1]. It contains 13-29 % inorganic components, of which 87-97 % is SiO_2 (silica) in an amorphous state [2]. The major impurities are Na, K, Mg, Ca and Fe whose presence as oxides and silicates can vary from 3 to 13 % in ash. They can be removed comparatively by acid-leaching, while life-time killing impurities such as Mo, Ti, Ta, Ni, V, Cr are either absent or present in very low concentrations and can also be similarly easily removed. Hence the importance of rice husk as a potential source for solargrade silicon [3]. Many investigators studied the structure of this ash-silica. Recently reports show that reasonably pure polycrystalline silicon can be prepared from rice husk white ash by a metallothermic reduction process [4]. Many applications of rice husk silica have been reported, focusing on a wide variety of products, e.g., metallurgical silicon, ceramics, zeolites, silicon tetrachloride, and cement/concrete applications [5]. An increasing application of rice husk is as fuel in heat generation for drying rice, due to its high calorific power (approximately 16,720 kJ/kg). In this combustion, rice husk ash (RHA) is produced. The burning of rice husk in air always leads to the formation of silica ash, which varies from gray to black depending on inorganic impurities and unburned carbon amounts [6]. The electrical property of silicon from rice husk ash are very sensitive to the presence of impurities, its electrical behavior is base on its inherent electronic structure [7]. Thermoelectric effect was discovered as early as 1821 by Thomas Johann Seebeck. This process is the direct conversion of temperature differences to electricity. During the following 120 years, great advances in both the theories and experiments were achieved. Thermoelectric energy conversion is an environmentally friendly technology with the potential for the energy supply of the future. Since the 1950s, studies in thermoelectric have developed very little, because of the painful difficulties in elevating the efficiency of these kinds of materials. The efficiency of thermoelectric materials is determined by a dimensionless parameter, figure of merit (ZT), where Z is given by $Z = \alpha^2\sigma/\kappa$ where T is the temperature, α is the thermoelectric power (or Seebeck coefficient), σ is the electrical conductivity, and κ is the thermal conductivity[8]. Bose et al. reported that 99.9 % purity polycrystalline silicon obtained from rice husk ash and high-purity magnesium powder. The materials in sintered pellet form was characterized for its structural, electrical, thermal, thermoelectric and other properties. A typical sintered pellet exhibited a room temperature (30 ^{o}C) thermoelectric power of 565 μVK^{-1} and an electrical resistivity of 35 Ωcm [9]. The best commercially available thermoelectric materials nowadays have a ZT around 1.0, which can be only used in some special cases. To be competitive to the kitchen refrigerators or air-conditioners, a ZT >= 3 at room temperature is required [10]. There are several studies of the preparation of silica from rice husk [11-18]. Real et al.[13] revealed that a homogeneous size distribution of nanometric silica particle could be prepared by heating rice husk at temperature of 873-1073 K in atmosphere of oxygen. Silica from rice husk ash has been used as a precursor for certain ceramic products and for silicon materials [17-18]. Conradt et al.[1] found that the particle size distribution of fumed silica could be obtained by burning rice husk at temperature of 600 °C in the atmosphere of air, oxygen, or steam. Liou [19] reported that uniformly sized ultrafine silica powder can be obtained by nonisothermal decomposition of rice husk in an oxidizing atmosphere. The characterization of silica prepared by heating the rice husk at various heating rate was performed. It was observed that the average pore diameter was 5.4 nm, and the average particle size was 60 nm. Silicon dioxide or silicon oxide nanostructures such as nanowires could be synthesized in many processes from silicon dioxide or silicon oxide source [20].

In this paper, we studied on the thermo-electrical properties of materials prepared by mixing silica from rice husk ash and carbon obtained from coconut shell charcoal and doped some metal oxide. The materials were studied in the thermoelectric properties and their microstructures.

2. Methodology

The rice husk ash amorphous silica was obtained by heated rice husk at 600 °C for 3 hrs, and mixed with amorphous carbon from heated coconut shell at 400 °C for 10 minutes and mixed with rice husks. The mixture was heated at 600 °C for 3 hrs. Then it was ground and heated again at 650 °C for 2 hrs. Some mixture was taken into the startle block and doping small amount of metal oxide, (Ge_2O_3, B_2O_3, P_2O_5) and grounded the mixture again, after that pressed into the pellets by using stainless steel block with pressure around 3 ton/cm^2.The pellets were heated at 700 °C in atmosphere of nitrogen for 1-3 hours. When the temperatures reached the setting points, the switch was turned off and to cool down to room temperature naturally. The pellets appear to become ceramics. The thermo-electrical property of ceramics pellets such as voltage and electromotive force with different temperature was carried out. We have observed the surface structure of some materials sources and products. The materials source and the specimens on the silicon substrates were examined by several techniques such as wavelength dispersive X-rays fluorescence (WDXRF), scanning electron microscope (SEM) and energy dispersive x-ray (EDX) with appropriate manners. The figures 1 and table 1 show the temperature of hot probe and difference of voltage between both sides of pellet samples and the compound of the mixtures. The table 2 presents the resistivity and Seebeck coefficient of the pellet samples. The figures 2-5 show the results of products which were prepared from the mixture of rice husk ash, graphite and GeO_2. The figures 6-9 show the results of products which were prepared from the mixture of rice husk ash, coconut shell charcoal and GeO_2.

3. Results and Discussion

The composition of the mixture samples (rice husk ash and coconut shell charcoal) was analyzed with the use of an X-ray fluorescence. The result of X-ray fluorescence of the mixture samples is shown in table 1. The data indicate the components of the mixture samples contain Na , Mg , Si , P , S , K , Ca , Mn , Fe and Cl . The intensity of Si peak is highest.

Table 1
The X-ray fluorescence analysis result

Analytic	Calibration Status	Compound Formula	Concentration (%)	Calculation Method
<Rb>	Not Calibrated	Rb_2O	0	Fixed
<Y>	Not free	Y_2O_3	0	Fixed
Na	Calibrated	Na_2O	0.143	Calculate
Mg	Calibrated	MgO	0.195	Calculate
Si	Calibrated	SiO_2	58.919	Calculate
P	Calibrated	P2O$_5$	2.143	Calculate
S	Calibrated	SO_3	0.680	Calculate
K	Calibrated	K_2O	30.666	Calculate
Ca	Calibrated	CaO	3.365	Calculate
Mn	Calibrated	MnO	0.906	Calculate
Fe	Calibrated	Fe_2O_3	0.771	Calculate
Cl	Calibrated	Cl	2.212	Calculate

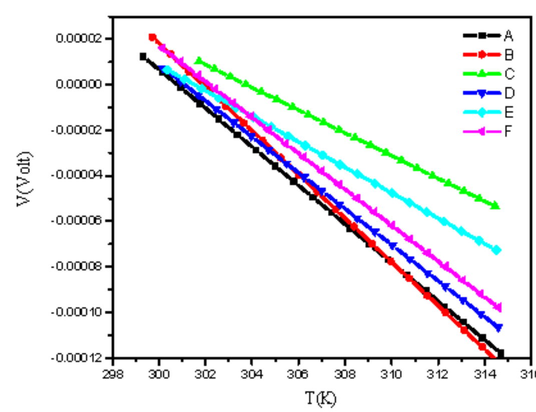


Figure 1. The temperature of hot probe and difference of voltage between both sides of pellet samples

pellet A y = -8.48E-06x+2.55E-03
pellet B y = -8.89E-06x+2.28E-03
pellet C y = -4.99E-06x+152E-03
pellet D y = -7.91E-06x+2.38E-03
pellet E y = -5.60E-06x+1.69E-03
pellet F y = -7.89E-06x +2.38E-03

In the figure 1, X-axis represents the temperature of hot probe and Y-axis represents the difference of voltages between both sides of pellet samples when different temperatures are applied on both sides of them. The voltages between both sides of samples were observed and recorded. The electromotive force was measured. The thermo-electrical property of the pellets, the Seebeck coefficient can be obtained by computer processing, graph and slope as shown in Table 2. We applied current to the pellet samples for measurement the voltage (*V*) and calculated the resistant (*R*), by Van der Pauw method [21]. The resistivities (ρ) of pellet samples were calculated based on the resistant and the sample dimensions.

We prepared six samples A, B, C, D, E and F by differential methods, follow as: Pellet A is prepared from rice husk ash mixed with B_2O_3 and it was pressured at 3 ton then heated at the temperature of 700 °C in atmosphere of nitrogen for 3 hrs. Pellet B is prepared from rice husk ash doped with GeO_2 at the middle of layer and it was pressured at 3 ton then heated at 700 °C in atmosphere of nitrogen for 3 hrs. Pellet C is prepared from rice husk ash doped with GeO_2 at the middle of layer and it was pressured at 3 ton then heated at 700 °C in atmosphere of nitrogen for 1 hr. Pellet D is prepared from rice husk ash mixed with GeO_2 for one side and another side rice husk ash mixed with B_2O_3 then it was pressured at 3 ton and then heated at 700 °C in atmosphere of nitrogen for 3 hrs. Pellet E is prepared from rice husk ash mixed with GeO_2 for one side and another side rice husk ash mixed with B_2O_3 then it was pressured at 3 ton and then heated at 700 °C in atmosphere of nitrogen for 1 hr. Pellet F is prepared from rice husk ash mixed with B_2O_3 and it was pressured at 3 ton then heated at the temperature of 700 °C in atmosphere of nitrogen for 1 hr. We used Van der Pauw method [22] and Ohm's law for calculating the resistivity of pellets. By equation R = V/I, where R is the resistant, V is the voltage and I is the current. We applied voltage and current to both side of the pellets for calculated the resistant. The resistivity (ρ) of the pellets can be calculated by following equations

$$\rho = \frac{\pi d}{\ln 2} \frac{(R_1 + R_2)}{2} f \qquad (1)$$

where $f \approx 1 - \left(\frac{Q-1}{Q+1}\right)^2 \frac{\ln 2}{2} - \left(\frac{Q-1}{Q+1}\right)^4 \left\{\frac{(\ln 2)^2}{4} - \frac{(\ln 2)^3}{12}\right\}$ (2)

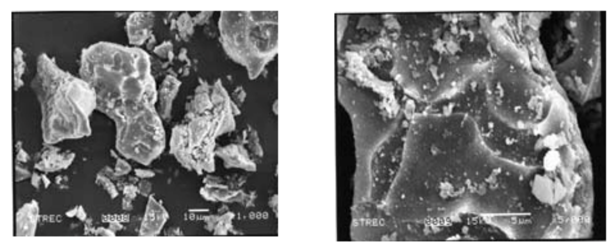
and ratio(Q) = $\left|\frac{R_{max}}{R_{min}}\right|$ (3)

The resistivity and Seebeck coefficient are shown in table 2. The table 2, we found that the Seebeck coefficient of pellets B is highest and C is lowest. The resistivity of pellets B is highest. The table 2 showed Seebeck coefficient and resistivity of each pellets no responding.

Table 2
The resistivity and Seebeck coefficient of the pellet samples

Samples	Resistivity (Ω.cm)	Seebeck coefficient (V/K)
A	153.264	8.48
B	342.032	8.89
C	271.880	4.99
D	106.091	8.48
E	139.130	7.91
F	322.771	5.60

The microstructure of materials source and the products on the substrates can be shown by scanning electron microscope (SEM) and energy dispersive x-rays (EDX). The figure 2 (a) and (b) showed the SEM images of materials sources prepared from rice hush ash mixed GeO_2 and graphite for assisting then heated in the atmosphere of nitrogen.



a b

Figure 2. SEM images of materials source prepared from burning rice husk ash mixed GeO_2 and graphite heated in atmosphere of nitrogen

The graph in the figure 3 shows EDX curve of materials source in figure 2. The EDX showed the compounds of materials source. We found many elements such as C, O, Ge, Si, Zn, Cu and Au. Au and Cu may result from gold coating and grid of equipment.

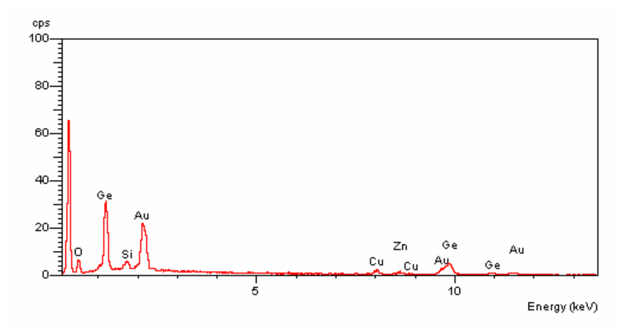
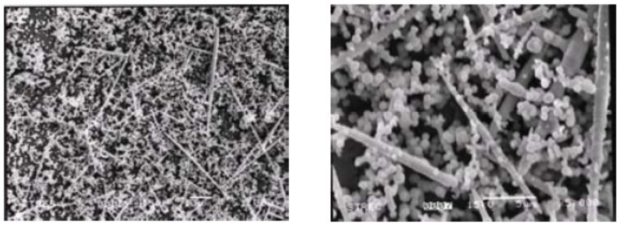


Figure 3. EDX image of materials source from figure 2

The figure 4 shows the SEM image of products on silicon substrates. SEM image reveals the synthesis of the structure of nanorods and nanoparticle-chain on the substrate, Fig.4 (b) is expansion image of Fig.4 (a).



a b
Figure 4. SEM image of the products on silicon substrate, (b) is the expansion of image (a).

The figure 5 shows EDX curve of the products on silicon substrate. EDX curve shows the compounds of microstructure of SEM image in figure 4 and shows many elements such as O, Ge, Si and Au. The peak of Au may be came from gold coating.

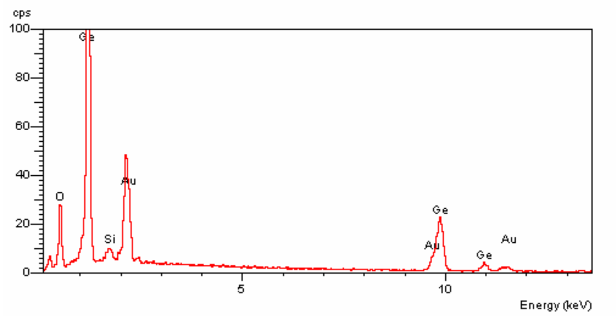
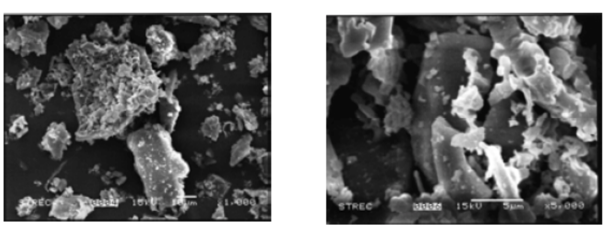


Figure 5. EDX curve of products on silicon substrate from figure 4

We used coconut shell charcoal replace graphite for catalysis. The materials source prepared from rice husk ash mixed GeO_2 and coconut shell charcoal then heated in atmosphere of nitrogen. Figure 6 showed SEM image of this sample. The surface of this sample is still look like the sample in figure 2.



a b
Figure 6. SEM image of materials source prepared from burning rice husk ash mixed GeO2 and coconut shell charcoal in atmosphere of nitrogen, (b) is expansion of image (a)

We investigated the compound of this materials source from figure 6. EDX curve in figure 7 shows many elements such as O, Ge, Si, Zn, Au and Cu. Au and Cu may derive from gold coating and grid of equipment. We can not observe carbon from this sample.

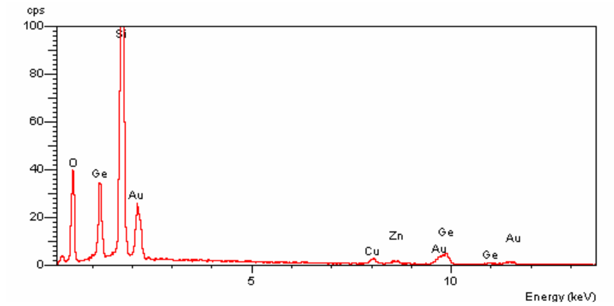
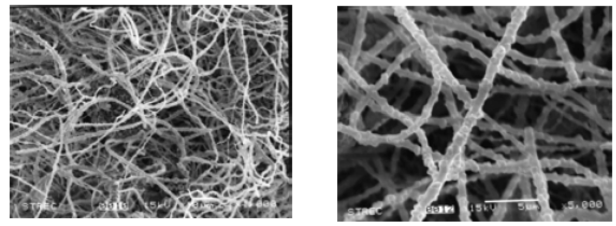


Figure 7. EDX curve of materials source in figure 6



a b
Figure 8. SEM image of the products on silicon substrate form materials source in figure 6. (a) magnification x 1000 (b) magnification x 5000

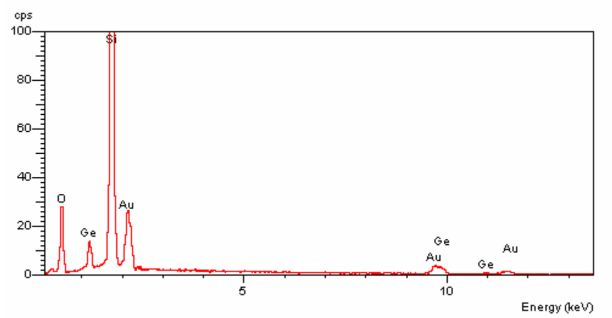


Figure 9. EDX curve of nanostructure materials in figure 8

The SEM images and EDX curves from Fig. 2-9 show the comparison of source materials and products on silicon substrates. They reveal that rice hush ash and coconut shell charcoal can be used to syntheses nanothermoelectric materials.

4. Conclusion

In summary, from the experimental results we conclude that the materials prepared from rice husk ash and coconut shell charcoal mixed with several metal oxides such as Ge_2O_3, B_2O_3 and P_2 O_3 may be used as thermoelectric materials. The products of the nanofibers and nanowires thermoelectric materials can be synthesized by heating mixture of rice husk ash, coconut shell charcoal or graphite and GeO_2 in atmosphere of nitrogen. The structures of these products have been characterized by X-rays fluorescence (XRF), scanning electron microscope (SEM), and energy dispersive X-rays (EDX) with appropriate manners. This result is the first report in making nanowires from waste agricultural products and these nanostructured materials may be utilized in future applications in nanotechnology.

Acknowledgements

The authors would like to thank Ubon Ratchathani University. We gratefully thank the Commission on Higher Education (CHE) and the Thailand Research Fund (TRF) for financial support and thank Dr. Somchai Kietgamolchai from Chularongkorn University for allowing us use equipments.

References

[1] R. Conradt, P. Pimkhaokham and U. Leela-Adisorn, Nano-structured silica from rice husk, *Journal of Non-Crystalline Solid 145*, 1992, 75-79.

[2] Y.Shinohara and N. Kohyama, Quantitative analysis of tridymite and crystobalite crystallized in rice husk ash, *Industrial Health, 42*, 2004, 277-285.

[3] D.N. Bose, P.A. Govindachargulu and H.D. Banerjee, Large grain polycrystalline silicon from rice husk, *Solar Energy Materials, 7*, 1982, 319-321.

[4] A. Chakraverty, P. Mishra, and H.D. Banerjee, Investigation of combustion of raw and acid-leached rice husk for production of pure amorphous white silica, *Journal of Materials Science, 23*, 1988, 21-24.

[5] K. Mochidzuki, A. Sakoda, M. Suzuki, J. Izumi, and N. Tomonaga, Structural behavior of rice husk silica in pressurized hot-water treatment process, *Industry Engineering Chemistry Research, 40*, 2001, 5705-5709.

[6] V.P. Delta, I.Kuhn, D. Hotza, Rice husk ash as an alternate source for active silica production, *Materials Letters, 57*, 2002, 818-821.

[7] T.H. Liou, F.W. Chang and J.J. Lo, Pyrolysis kinetics of acid-leached rice husk, *American Chemical Society, 60*, 1997, 568-573.

[8] L.I. Anatychuk, S.V. Melnichuk, and S.V. Kosayachenko, Thermoelectric properties of superlattices Si/Ge , *Proc.17th IEEE Conf. on Thermoelectrics*, Nagoya, Japan, 1998, 93-96.

[9] S. Bose, H.N. Acharya and H.D. Banerjee, Electrocal, thermal, thermoelectric and related properties of magnesium silicide semiconductor prepared from rice husk, *Journal of Materials Science*, *28*(20), 1993, 5461-5468.

[10] Qiu, Xiaofeng; *Burda, Proc.4th SPIE. on Clemens Physical Chemistry of Interfaces and Nanomaterials*, *5929*, 2005, 243-249.

[11] James A. Amick, Purification of rice hulls as a source of solar grade silicon for solar cell, *Journal of Electrochemistry Soc*iety, *29*(4), 1982, 864-866.

[12] L.P. Hunt, J.P.Dismukes, J.A. Amick, Rice hulls as a raw materials for producing silicon, *Journal of Electrochemistry Soc*iety, *131*(7) 1984, 1683-1686.

[13] C. Real, M.D. Aleala, J.M. Criado, Preparation of silica from rice husk, *Journal of American Ceramics Society, 79*(8), 1996, 2012-2016.

[14] P. Mishra, A. Chakraverty, H.D. Banerjee, Production and purification of silicon by calcium reduction of rice-husk white ash, J*ournal of Materials Science, 20*, 1985, 4387-4391.

[15] M. Patel, A. Karera, P. Prasanna, Effect of thermal and chemical treatments on carbon and silica contents in rice husk, *Journal of Materials Science, 22*, 1987, 2457-2464.

[16] A. Chakraverty, P.Mishra, H.D. Banerjee, Investigation of combustion of raw and acid-leached rice husk for production of pure amorphous white silica, *Journal of Materials Science, 23*, 1988, 21-24.

[17] A. Oya, N. ki shimoto, S. Mashio, K. Kumakura, T.Suzuki, Structure and properties of moulded carbon derived from rice hull, *Journal of Materials Science, 30*, 1995, 6249-6252.

[18] T.H.Liou, F. W. Chang, J.J. Lo, Pyrolysis kinetics of acid-leached rice husk, *Industry Engineering Chemistry Research, 60*, 1997, 568-573.

[19] Tzong-Horng Liou, Preparation and characterization of nano-structured silica from rice husk, *Materials Science and Engineering A364,* 2004, 313-323.

[20] B.K. Teo, C.P. Li, X.H. Sun, N.B. Wong and S.T. Lee, Silicon-silica nanowires, nanotubes, and Biaxial nanowires: inside, outside, and side-by-side growth of silicon versus silica on zeolite, *Inorganic Chemistry, 42*, 2003, 6723-6728.

[21] L.J. van der Pauw, A method of measuring specific resistivity and hall effect of discs of arbitrary shape, *Philips Research Reports,. 13*(1), 1958, 1-9.

[22] A. A. Ramadan, R. D. Gould, And A Ashour., On the van der Pauw method of resistivity measurements, *Thin solid films, 239*, 1994, 272-275.