Nano World Journal

https://doi.org/10.17756/nwj.2017-047

Research Article

Open Access

Effect of Thermal Annealing on the Optical and Structural Properties of the a-SiC Thin Films Deposited by DC Magnetron Sputtering

Saloua Merazga[1*], A. Keffous[1], A. Brighet[2], M. Kechouane[2]

[1]CRTSE, Division Couches Minces Surfaces et Interfaces, 02 Bd Frantz Fanon, BP 140 Alger 7-merveilles, Alger, Algeria
[2]Université des Sciences et de la Technologie Houari Boumediene, Faculté de Physique, BP 32 El Alia, 16111, Alger, Algeria

[*]Correspondence to:
Saloua Merazga, PhD
CRTSE, Division Couches Minces Surfaces et Interfaces, 02 Bd Frantz Fanon, BP 140 Alger 7-merveilles, Alger, Algeria
E-mail: merazgas@yahoo.fr

Received: January 19, 2017
Accepted: September 18, 2017
Published: September 21, 2017

Citation: Merazga S, Keffous A, Brighet A, Kechouane M. 2017. Effect of Thermal Annealing on the Optical and Structural Properties of the a-SiC Thin Films Deposited by DC Magnetron Sputtering. *NanoWorld J* 3(3): 54-58.

Published by United Scientific Group

Abstract

Hydrogenated Amorphous silicon carbide (a-SiC:H) thin films were prepared by DC magnetron sputtering technique using 6H-SiC polycrystalline target in a mixture of $H_2$and Ar gas. They were thermally annealed at various temperatures up to 800 °C. The a-SiC:H films were deposited at different hydrogen partial pressure rates varying from 0 to 9 sccm on p-type Si(100) and Corning glass 9075 substrates. The annealing temperatures were varied and the samples were characterized by Infrared spectroscopy (FTIR), Raman spectroscopy and Ellipsometry spectroscopy. The previous results of infrared and Raman spectroscopy reveal structural modifications in the material structure of the layers through a reduction of the thickness and optical gap and the variation of the refractive index during the annealing.

Keywords

Amorphous SiC, Annealing, Sputtering, DC magnetron, Gap

Introduction

Annealing of hydrogenated silicon carbide (a-SiC:H) thin films has attracted great interest in optoelectronics and photovoltaic domain [1] for the films prepared by plasma enhanced chemical vapor deposition(PECVD), due to their chemical stability and interesting optical and electronic properties. This type of material has a major advantage, which consists of its possibility to modify its properties by either varying the preparation conditions or the film composition [2, 3].

The annealing effect on a-Si_xC_{1-x}:H thin films have been reported by several authors [2-5]. A.L. Baia Neto et al. reported the decrease of Si-H bonds at low annealing temperatures, whereas the C-H bonds are only affected at temperatures higher than 500 °C. On near stoichiometric a-SiC:H films deposited using a RF glow discharge system. M. Kuenle et al. investigated that the deposited films became amorphous directly after deposition and nanocrystalline after annealing at 1300 °C. Thereabout, D. H. Yoon founded that an annealing process results in structural rearrangement and evacuation of hydrogen atoms from CH_n and SiH_n bonds. However, F. Demichelis and G. Kaniadakis reported that the optical parameters of a-SiC:H films deposited by sputtering system strongly depend on the preparation conditions and appear to be sensitive functions of the network disorder [6].

However, the influence of preparation conditions on the thermal stability of amorphous SiC:H films remain unclear up to now.

All these investigations are carried out in order to show the great importance of the thermal treatment study of the a-SiC:H. Many phenomena can occur

during thermal annealing of a-SiC:H, such as hydrogen emission and structure rearrangement that affect the properties of the amorphous material and its applications [7].

In fact, studies of these films showed that most of the hydrogen leaving the material occurs after annealing below 500 °C and that the transition from the amorphous state (a-SiC:H) to the polycrystalline state (poly-SiC) happens above 650 °C. At this temperature, the layers become a mixed phase material comprising size of submicron crystallites embedded in the amorphous matrix [8, 9]. Never the less, the crystallization of a-SiC:H prepared by PECVD is started at annealing temperatures greater than 1100 °C [10].

In the light of all these interesting works, our work focuses on the effect of thermal annealing (500–800 °C) on the structural and optical properties (optical gap, thickness) of a-SiC films deposited by DC magnetron sputtering process (SP). Our results confirm that the annealing induced enhancement of the optical properties of the a-SiC films which correlated with the structural modifications of the thin films.

Experimental procedure

The a-SiC:H thin films were deposited by DC magnetron sputtering (SP) of 6H-SiC target in Ar and H_2 gas mixture. Under these experimental conditions: the substrate temperature was 250 °C, plasma power is 130W; the distance target-substrate is 3.5 cm and the Argon flow rate was 5 sccm with different hydrogen flow rates at total pressure of 10^{-5} mbar. The full parameters of the deposition process were shown in the Table 1.

Table 1: Deposition parameters of the a-SiC:H layers.

Samples	D_{H2} (sccm)	Temperature (°C)	Time of deposition (min)	Plasma power (W)	D_{Ar} (sccm)	P_{tot} (mbar)
E0	0	250	60	130	5	10^{-5}
E3.5	3.5	250	60	130	5	10^{-5}
E7	7	250	60	130	5	10^{-5}
E9	9	250	60	130	5	10^{-5}

In order to study the effect of thermal annealing on the microstructure and to improve the properties of our films, a thermal annealing was performed using a furnace of Barnstoad type that can reach up to temperatures of 1200 °C under high vacuum (10^{-7} mbar) using a turbo molecular pump. This oven is equipped with a quartz tube in which the samples are inserted. Since, Quartz has a glass transition at 1200 °C, we limited ourselves to annealing at 800 °C for 1 hour. This thermal treatment was prepared under the following conditions (Table 2).

We will consider in particular the structural properties of a-SiC:H thin layers, such as the nature of chemical bonds and the composition or the degree of crystallization. For each of the characterization techniques used, we looked at the influence of thermal treatment on the optical properties of the layers.

Table 2: Annealing conditions of a-SiC:H thin films.

Sample	H_2 Flow rate D_{H2} (sccm)	Annealing temperature – 1 hour Pressure 10^{-5} mbar
E0	0	800
E3.5	3.5	700
E7.5	7.5	500
E9	9	600

Fourier transform infrared spectroscopy (FTIR) was performed by using a *CARY 500 – VARIAN spectroscopy* ranging from 400 to 4000 cm^{-1}. On the other hand, the Raman spectra were performed by using a Raman spectroscopy. The optical measurements were performed in the spectral range between 200 and 900 nm by *Semilab-Spectroscopic Ellipsometry Analyzer – SEA.*

Results and Discussion

Optical measurement

Using the Ellipsometry spectroscopy of *Semilab Analyzer – SEA type,* we can estimate the optical parameters (optical gap E_g, refractive index ns, thickness) of the annealing films. The experimental spectrum is modeled using iterative simulation for adjusting the model parameters from the Tauc-Lorentz law in order to estimate the gap and the thickness of the layer.

Figure 1 shows the variation of the optical gap before and after thermal annealing at 500-800 °C with a step of 100 °C. Indeed, the optical gap of the sample E3.5 sccm is varied from 2.30 to 1.40 eV after annealing at 800 °C. This value is quite low for photovoltaic application. These results are in agreement with the work of Y.T. Kim et al. [7] on the annealing effect of a-SiC:H layers. This gap increase in fact due to the replacement of the -Si-Si bonds by creating a crystalline phase ß-SiC when the annealing temperature nears 700 °C. Above this temperature, the value of the optical gap decreases because in this state the material approaches

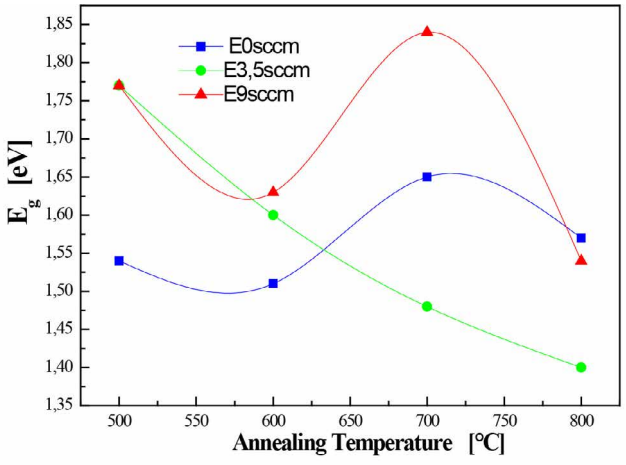

Figure 1: Evolution of the optical gap (E_g) of the deposited films as a function of the annealing temperature.

the polycrystalline SiC. Therefore, this temperature (800 °C) seems to be that in which the sample reaches almost its final state [6]. On the contrary, for the non-hydrogenated sample (E0 sccm) we observe that the gap remains practically constant with a value around 1.5 eV. It is surprising to not observe a real gap change for this sample.

Figure 2 shows the change in thickness depending on the deposition temperature for the different samples (E3.5 sccm, 7.5 sccm, and 9 sccm), where we observe a decrease of the thickness for all the samples after annealing, which is due to the structure modifications of the material.

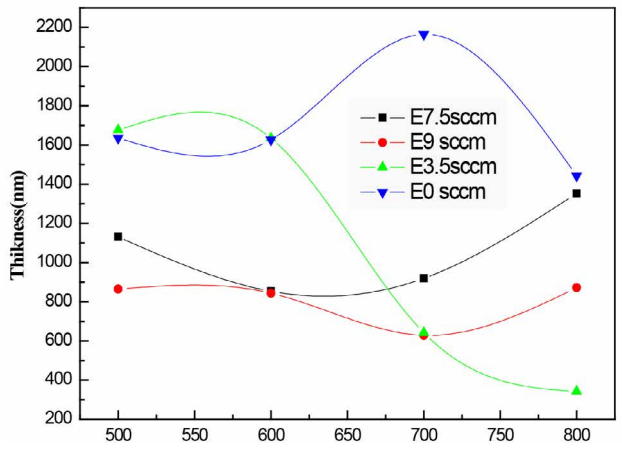

Figure 2: Evolution of the films thickness as a function of the annealing temperature.

In Figure 3, the evolution of the refractive index of the annealed layers shows two opposing tendencies, an increase or stability depending in the nature of the sample, where the refractive index of the sample (E0 sccm, E9 sccm) remains practically constant after the thermal annealing. Certainly, this tendency parameter for the other samples (E3.5 sccm, E7.5 sccm) has been known to increase following the thermal annealing. This can be explained by the decrease in the hydrogen content and then an increase in macroscopic density which renders the material to become more transparent.

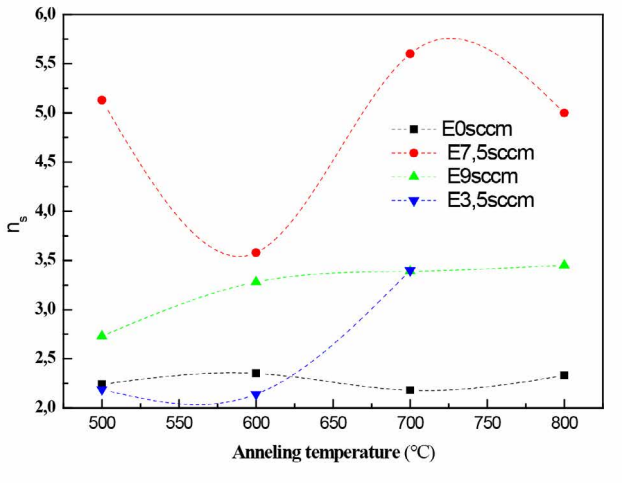

Figure 3: Evolution of the refractive index (n_s) of the deposited films as a function of the annealing temperature.

Structural characteristics

FTIR spectroscopy:

Figure 4A and 4B shows the infrared absorption spectra of the samples (E0 sccm, E3.5 sccm) annealed at 500, 600, 700 and 800 °C respectively. The absorbance is normalized by the thickness layers after annealing.

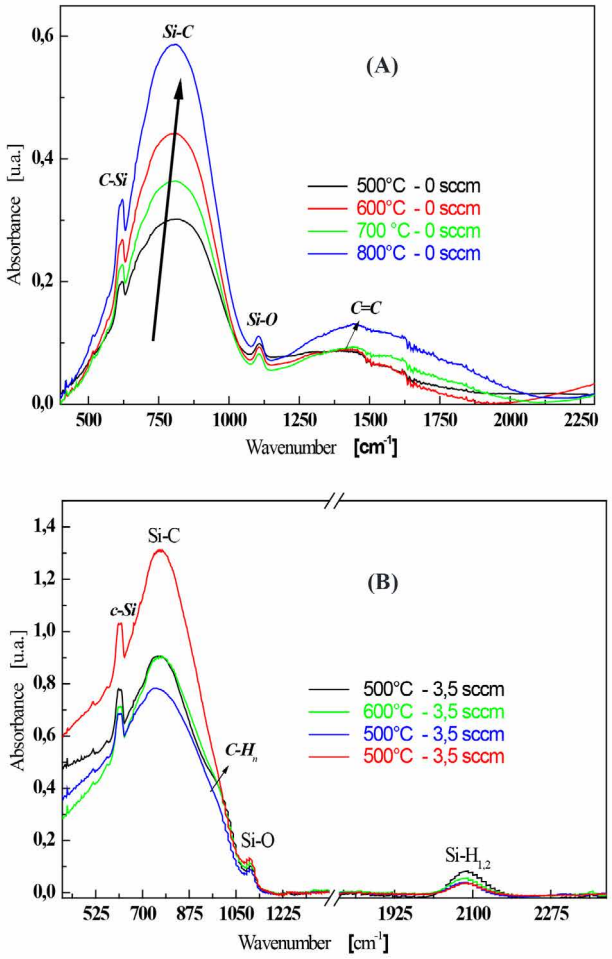

Figure 4: The infrared absorption spectra of the: **(A)** E0 sccm sample, **(B)** E3.5 sccm sample annealed at 500, 600, 700 and 800 °C for 60 min.

The FTIR measurements were achieved in order to investigate the change in binding structures of the different a-SiC films.

The peak at 780 cm^{-1} is due to the stretching modes of Si-C for the non-hydrogenated sample, but not necessarily for the sample E3.5 sccm. While this band is narrower and intense at 800 °C and broader and less intense at 700 °C, one conger confused when it comes to rocking modes (wagging) and rotation (rocking) of C-H_n groups between 950 and 1050 cm^{-1}; especially with the increase in the intensities following the annealing temperature. The peak at 1100 cm^{-1} corresponds to the optical transverse elongation (TO) of Si-O bonds in a carbide environment [11].The bond at 1590 cm^{-1} is due to aromatic stretching mode of C=C [12], whereas the bond at 620 cm^{-1} is due to crystalline mode (c-Si) [13]. The peak at 2100 cm^{-1} is attributed to the elongation of Si-H mode where

the silicon atom is linked to 1, 2 or 3 carbon atoms (E3.5 sccm) [14].

The significant increase in the peak intensity at 780 cm^{-1} with the increase in annealing temperature shows that many Si-C bonds are created due to the dissociation of the Si-H_n and C-H_n under the effect of temperature. This phenomenon of dehydrogenation involves also a structural rearrangement of the material, which is clearly seen at the evolution of the peak (780 cm^{-1}) corresponding to the Si-C bonds. This also probably increases the number of C=C liaisons (and to a lesser extent Si-Si) during annealing but these homopolar bonds cannot be easily detected by infrared spectroscopy. As then the intensity increases; we observe a narrowing of the peak absorption at 780 cm^{-1}. This is the signature of a disorderly decline in the amorphous network. It is generally known that during the crystallization of a SiC phase, the form of the absorption peak of Si-C turns of a Gaussian function in a Lorentzian function [15]. In addition, the shift of this peak to high energies (810 cm^{-1}) and the reproduction of the half-height width indicate a transition from the amorphous state to the crystalline state. These observations are made significantly on the spectrum related to non-hydrogenated layers (E0 sccm). However, it will not be possible to confirm from these infrared spectra that there's a possibility of crystallization of these layers.

The absence of the Si-H bond at 2100 cm^{-1} for a non-hydrogenated sample (E0 sccm) that there's not enough hydrogen to form the bond at 2000 cm^{-1}. However, this bond is indicated in the hydrogenated sample (E3.5 sccm) with decreased intensities following the increase of the annealing temperature. For the same sample (E3.5 sccm), we see that all the peaks corresponding to hydrogen bonds (Si-H, Si-Hn, C-Hn, Si-CH3) decrease. This indicates an important or even the total desorption of hydrogen from the layer during annealing. The presence of the Si-O bond at 1100 cm^{-1} with a decreased intensity due to the increase of the annealing temperature, highlights an oxidation of the layers both before and after annealing. Here we see that the oxygen is also present within the layer and cannot; therefore, be derived from a simple oxidation in the air. In general, the presence of oxygen is related to the deposition process of the thin layer and the presence of oxygen contamination in the bell.

Raman spectroscopy

To better understand the evolution of the structure based layers with the varying annealing temperatures, Raman spectroscopy measurements were performed. Raman spectra of the samples (E0 sccm) are shown in Figure 5 indicate the presence of a wide significant peak around 1430 cm^{-1} which attributed to the C=C bond in the film with an intensity that increases as a function of the annealing temperature. It is particularly interesting that the vibrational modes of carbon subnet appear in the Raman spectra as a symmetric Gaussian band around 1450 cm^{-1} [3]. This peak is remarkable because the maximum of the photon energy of a one of crystalline polytypes at 970 cm^{-1}. Another band around 960 cm^{-1} is assigned to the second optical transverse mode (TO) of amorphous silicon [17]. While, the homopolar bonds were assigned to the asymmetric peak at 520 cm^{-1} in this spectrum [18], it is slightly higher than the peak at 480 cm^{-1} in the Raman spectrum of a-SiC. This peak is still below that at 520 cm^{-1} of c-Si. We believe that the shift of Si-Si peak is due to the presence of ß-SiC crystalline phase with a density of vibration states which does not appear in the Raman spectrum of a-SiC according to the prescription of Smith [16]. The amount of these crystalline phases' increases under thermal annealing; therefore, this shift is the thermal annealing effect on the amorphous material.

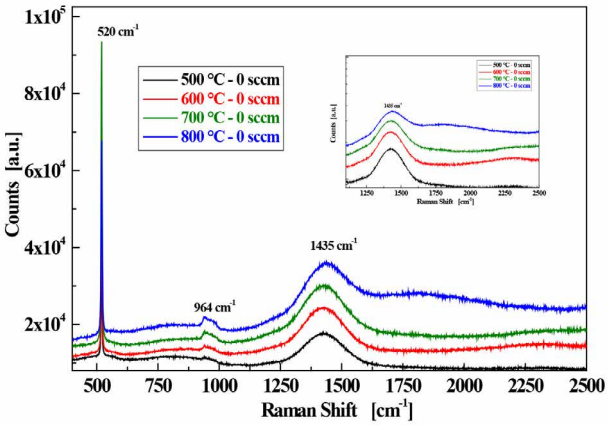

Figure 5: Raman spectra of the E0 sccm sample annealed at 500, 600, 700 and 800 °C for 60 min.

Conclusion

In this contribution, we have studied the evolution of optical parameters (optical gap, the refractive index, thickness) and the structural changes of the a-SiC films deposited by DC magnetron sputtering technique following the thermal annealing. The increase of the temperature, until 700 °C, produces an increase of the optical gap. Above this temperature it decreases because in this state the material approaches the polycrystalline SiC. The modification in the material structure results from a change in the thickness and refractive index, causing an increase in macroscopic density of the layers during the annealing. From FTIR spectra, we observed a shift of the peak to high energies (810 cm^{-1}) and the reproduction of the FWHM indicate a transition from the amorphous state to the crystalline state. The Raman spectra confirm that the quantities of the crystalline phases increase under thermal annealing; which makes this peak becomes more intense following the annealing temperature.

Acknowledgments

This work was supported by the National Research Fund of DG-RSDT / MESRS from Algeria (FNR11_13 UDTS).

References

1. Song D, Cho E, Cho Y, Conibeer G, Huang Y, et al. 2008. Evolution of Si (and SiC) nanocrystal precipitation in SiC matrix. *J Thin Solid Films* 516(12): 3824-3830. https://doi.org/10.1016/j.tsf.2007.06.150
2. Awad Y, El Khakani MA, Brassard D, Smirani R, Camiré N, et al. 2010. Effect of thermal annealing on the structural and mechanical properties of amorphous silicon carbide films prepared by polymer-source chemical vapor deposition. *J Thin Solid Films* 518(10): 2738-2744. https://doi.org/10.1016/j.tsf.2009.10.154

3. Baia Neto AL, Camargo Jr SS, Carius R, Finger F, Beyer W. 1999. Annealing effects on near stoichiometric a-SiC:H films. *J Surface and Coatings Technology* 120-121: 395-400. https://doi.org/10.1016/S0257-8972(99)00390-4
4. Kuenle M, Janz S, Eibl O, Berthold C, Presser V, et al. 2009. Thermal annealing of SiC thin films with varying stoichiometry. *J Materials Science and Engineering B* 159-160: 355-360. https://doi.org/10.1016/j.mseb.2008.10.056
5. Yoon DH, Suh SJ, Kim YT, Hong B, Jang GE. 2003. Influence of Hydrogen on a-SiC: H Films Deposited by RF PECVD and Annealing effect. *J The Korean Physical Society* 42: S943-S946.
6. Demichelis F, Kaniadakis G. 1992. Structural evolution in a-SiC:H induced by thermal annealing as deduced by optical properties. *Physica B: Condensed Matter* 179(1): 59-64. https://doi.org/10.1016/0921-4526(92)90621-X
7. Kim YT, Cho SM, Hong B, Suh SJ, Jang GE, et al. 2002. Annealing Effect on the optical properties of a-SiC:H deposited by PECVD. *Materials Transactions* 43(8): 2058-2062. https://doi.org/10.2320/matertrans.43.2058
8. Carbone A, Demichelis F, Kaniadakis G. 1991. Annealing temperature dependence of the optical properties of sputtered hydrogenated amorphous silicon carbide. *J Non-Crystalline Solids* 128(2): 139-145. https://doi.org/10.1016/0022-3093(91)90506-2
9. Demichelis F, Crovini G, Pirri CF, Tresso E, Giamello E, et al. 1991. Hydrogen evolution in amorphous silicon carbide. *Physica B: Condensed Matter* 17(1): 149-152. https://doi.org/10.1016/0921-4526(91)90118-X
10. Gharbi R, Fathallah M, Pirri CF, Tresso E, Crovini G, et al. 2000. Properties of a-SiC: H films and solar cells. *J Canadian of Physics* 77(9): 699-704. https://doi.org/10.1139/p99-021
11. Teresa O, Choi CK. 2010. Comparison between SiOC thin films fabricated by using plasma enhance chemical vapor deposition and SiO_2 thin films by using fourier transform infrared spectroscopy. *J The Korean Physical Society* 56(4): 1150-1155.
12. Shaik H, Thulasi Raman KH, Mohan Rao G. 2012. Influence of Si-C bond density on the properties of a-$Si1_{-x}C_x$ thin films. *Appl Surf Science* 258(7): 2989-2996. https://doi.org/10.1016/j.apsusc.2011.11.024
13. Akaoglu B, Sel K, Atilgan I, Katircioglu B. 2008. Carbon content influence on the optical constants of hydrogenated amorphous silicon carbon alloys. *Optical Materials* 30(8): 1257-1267. https://doi.org/10.1016/j.optmat.2007.06.005
14. Ambrosone G, Coscia U, Ferrero S, Giorgis F, Mandracci P, et al. 2002. Structural and optical properties of hydrogenated amorphous silicon-carbon alloys grown by plasma enhanced chemical vapour deposition at various rf powers. *Phil Mag Part B* 82(1): 35-46. https://doi.org/10.1080/13642810208211214
15. Rajagopalan T, Wang X, Lahlouh B, Ramkumar C, Partha D, et al. 2003. Low temperature deposition of nanocrystalline silicon carbide films by plasma enhanced chemical vapor deposition and their structural and optical characterization. *J Applied Physics* 94(8): 5252. https://doi.org/10.1063/1.1609631
16. Chen T, Kohler F, Heidt A, Huang Y, Finger F, et al. 2011. Microstructure and electronic properties of microcrystalline silicon carbide thin films prepared by hot-wire CVD. *Thin Solid Films* 519(14): 4511-4515. https://doi.org/10.1016/j.tsf.2011.01.336
17. Gorman M, Solin SA. 1974. Direct evidence for mononuclear bonds in amorphous SiC. *Solid State Communications* 15(4): 761-765. https://doi.org/10.1016/0038-1098(74)90256-7
18. Smith Jr. JE, Brodsky MH, Crowder BL, Nathan MI, Pinczuk A. 1971. Raman spectra of amorphous Si and related tetrahedrally bonded semiconductors. *Phys Rev Lett* 26: 642. https://doi.org/10.1103/PhysRevLett.26.642