



17 April 1998

**CHEMICAL
PHYSICS
LETTERS**

Chemical Physics Letters 286 (1998) 508–514

Covalent bonding of thiophenes to Si(111) by a halogenation/thienylation route¹

J. He, S.N. Patitsas, K.F. Preston, R.A. Wolkow, D.D.M. Wayner

Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa K1A 0R6, Canada

Received 10 November 1997; in final form 26 January 1998

Abstract

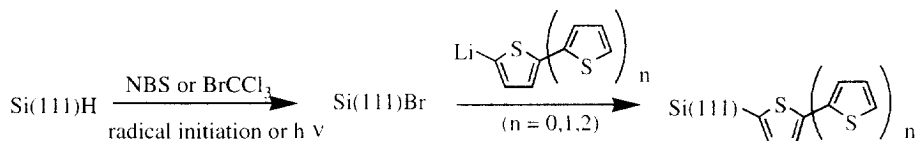
Thienyl monolayers covalently bonded to a Si(111) surface were prepared by a wet chemical process in which a Si(111)-H surface was brominated to form Si(111)-Br and further reacted with lithiated thiophenes. Both *N*-bromosuccinimide and bromochloroform were found to be effective brominating reagents. The derivatized Si(111) surfaces were characterized by XPS, AES, ATR-FTIR and NEXAFS. © 1998 Elsevier Science B.V.

1. Introduction

The covalent attachment of an organic monolayer to a semiconductor surface provides a means of passivation and, more significantly, offers a potentially important new methodology for the incorporation of chemical and biological functionalities into solid-state devices. Not surprisingly, therefore, interest in the wet chemistry of semiconductor surfaces is growing rapidly. Notable recent successes in the controlled chemical modification of surfaces include alkyls and aryls on Si(111) [1–4], carboxylic acids and alcohols on porous silicon [5–10], alkylthiols on GaAs [11–15], and aromatic derivatives and thiols on InP [16–18]. In many of these examples, the surfaces were modified with long-chain alkyl groups which ideally will form densely packed monolayers that effectively inhibit the transfer of electrons or energy across the interface. The ability to create ordered organic monolayers that provide control of electron transport at the interface is an important milestone towards the fabrication of molecular-scale devices. Such monolayers will have applications in molecular sensing and as templates for the epitaxial growth of organic or metallo-organic films on semiconductors.

¹ Issued as NRCC Publ. No. 40854.

In this Letter, we report the chemical derivatization of the Si(111) surface with thiophenes using the following strategy.



The synthetic surface chemistry of single-crystal Si appears to parallel that of molecular organosilicon chemistry. Our work demonstrates that organic molecules with extended conjugation can be readily covalently attached to silicon surfaces by this procedure. Furthermore, it demonstrates one of the basic steps required to attach spatially discrete molecular wires [19] directly to the Si lattice at the semiconductor surface. The method leads to robust thiophene-based monolayers on Si(111).

2. Experimental section

Si(111) single crystals (1 $\Omega \cdot \text{cm}$, *n*-type) were cleaned in 3:1 concentrated $\text{H}_2\text{SO}_4/30\% \text{H}_2\text{O}_2$, 1:1 $\text{NH}_4\text{OH}/30\% \text{H}_2\text{O}_2$, followed by etching with 40% aqueous NH_4F (6 min), procedures that ensure atomically flat surfaces terminated by a monolayer of H atoms [20]. Bromination of the Si surface was accomplished by reaction of Si(111)-H with either *N*-bromosuccinimide (NBS) for 20 min at 60°C in *N,N*-dimethylformamide (DMF) solution with benzoyl peroxide as the radical initiator, or pure bromochloroform (CCl_3Br) under conditions such as thermolysis (80°C for 30 min), photolysis (300 nm UV for 20 min) or free-radical initiation (benzoyl peroxide at 60°C for 30 min). Chlorination of the Si(111)H surface was accomplished by reaction with molecular chlorine (2 Torr) using either thermal (80°C for 10 min) or photochemical (350 nm for 10 min) initiation. Exposure of Si(111)-Br/Cl to a solution of a lithiated thiophene (2-thienyllithium, 2-lithium-3-methylthiophene, 5-lithium-2,2'-bithiophene, 5-lithium-2,2':5',2''-terthiophene prepared by the reaction of the thiophene with *n*-butyllithium except for 2-thienyllithium which was commercially available) for several hours to 2 days depending on the number of thienyl units at 60°C yielded the thienyl-terminated Si surfaces. The derivatized surfaces were rinsed with THF, ethyl alcohol, and were then sonicated in dichloromethane for 5 min.

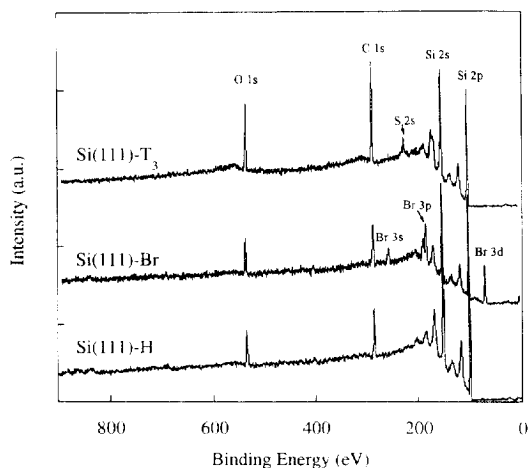


Fig. 1. X-Ray photoelectron survey spectra of H-, Br- and terthiophene (T_3)-terminated Si(111) surfaces. The main peaks observed are O 1s (532 eV), C 1s (285 eV), Br (257 eV), Br (183, 189 eV), Br (70 eV), Si (151 eV), and Si (100 eV).

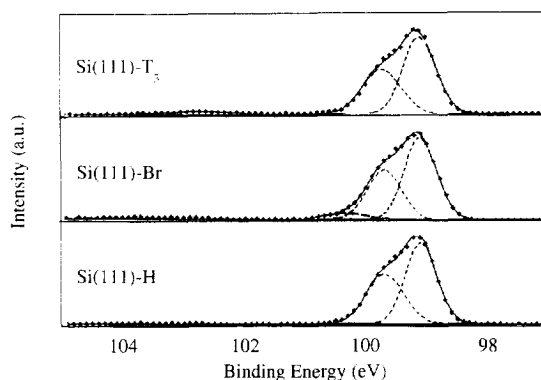


Fig. 2. High-resolution XPS spectra of the Si 2p region of H-, Br- and T₃-terminated Si(111) surfaces, with the same experimental conditions described in Fig. 1. ■, Data; ----, deconvolutions; and ———, resulting fits to the spectrum.

X-ray photoelectron spectra (XPS) were recorded on a Kratos Axis Instrument, using monochromated Al K α (1486 eV) radiation with detection on the surface normal. The pressure during analysis was about 5×10^{-8} Torr. Auger spectra were obtained using a commercial (Perkin–Elmer) spectrometer. The electron beam was unmodulated and directed normal to the sample surface. Back-scattered electrons were analyzed with a cylindrical mass analyzer. During the loading process the samples (which were prepared in an inert atmosphere) were exposed to air for about 5 min. Attenuated total internal reflectance (ATR)-FTIR spectra were recorded using a Nicolet MAGNA-IR 860 spectrometer at 4 cm^{-1} resolution. The ATR element was mounted in a purged sample chamber with the light focused normal to one of the 45° levels. Background spectra were obtained using a freshly oxidized Si(111) ATR element. Sulfur $L_{2,3}$ -edge near edge X-ray absorption fine structure (NEXAFS) spectra were measured using the Grasshopper monochromator beamline at the Canadian Synchrotron Radiation Facility (CSRF) at the University of Wisconsin at Madison (Madison, WI). Data were obtained using total electron yield detection [21].

3. Results and discussion

The starting Si(111)–H surface was shown to consist solely of monohydride normal to the surface from the single narrow absorption at 2083.4 cm^{-1} in the p -polarized attenuated total internal reflection (ATR) infrared (IR) spectrum. The absorption was not observed in the s -polarized spectrum. Exposure of Si(111)–H to a N,N -dimethylformamide solution of NBS using dibenzoyl peroxide as initiator generated the bromo-terminated surface. The NBS bromination of Si(111)–H is believed to be analogous to the allylic or benzylic free-radical bromination of alkanes or alkylbenzenes which is known to propagate by the generation of a low steady-state concentration of molecular bromine (Br₂) [22]. XPS confirmed the formation of Si(111)–Br through the peaks at 257 eV (Br 3s), 183 and 189 eV (Br 3p), and 70 eV (Br 3d) (Fig. 1). High-resolution XPS of the Si 2p of the modified surface showed, in addition to the substrate Si signal, a peak located at $\sim 0.90 \text{ eV}$ higher in binding energy (Fig. 2) the position and intensity of which are consistent with the formation of surface Si–Br bonds.² Similar observations have been made for surface Si–Cl bonds [3,23]. The presence of O and C peaks in the XP survey spectra for H–Si and Br–Si (Fig. 1) are likely due to carbonaceous contamination since the Si 2p high-resolution XPS spectra of Si(111)–H and Si(111)–Br (Fig. 2) do not indicate the formation of Si oxides

² Both H-terminated Si and thiophenes-terminated Si produced Si 2p spectra that were well-fit to a spin-orbit doublet of Si $2p_{3/2}$ and Si $2p_{1/2}$ in the expected 2:1 area ratio, 0.60 eV energy separation, and the peak position for lattice Si. However, bromination yielded an XPS spectrum which could only be well-fit by including a third peak at about 0.90 eV higher energy than the Si $2p_{3/2}$ peak, while holding the parameters of the substrate doublet constant. This is consistent with the formation of surface Si–Br bonds.

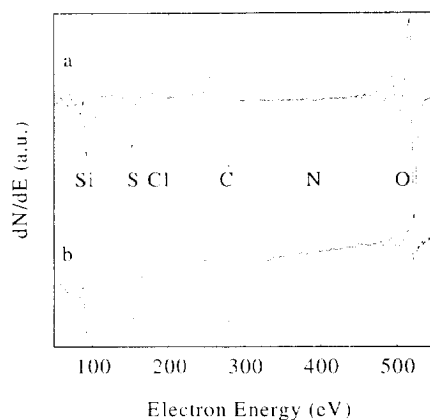


Fig. 3. Auger spectra of (a) Si(111)-T and (b) Si(111)-T₃. Both samples were prepared as described in the text from a chlorine terminated surface. The peaks observed: Si (92 eV), S (152 eV), Cl (183 eV), C (278 eV), N (392 eV) and O (522 eV). Plot (b) has been arbitrarily scaled. Incident electron beam energies were 3 keV for (a) and 1 keV for (b).

(i.e. absence of the peak at binding energy 102–104 eV). The brominated surfaces were only mildly moisture-sensitive and could be handled in air for several minutes without hydrolysis.

We find that CCl₃Br also is an effective brominating agent for Si(111)-H. The bromination reaction can be initiated by thermolysis, photolysis or free-radical initiation. Within the limits of detection of XPS, Br is the only halogen bound to the Si(111) surface (i.e. no detectable Cl). The Si(111) bromination chemistry is very similar to the molecular reaction of the structurally related tris(trimethylsilyl)silane with BrCCl₃, which takes place spontaneously at room temperature yielding tris(trimethylsilyl)bromosilane and chloroform [24].

Exposure of the Si(111)-Br or Si(111)-Cl to a solution of lithiated thiophene (T) or lithiated terthiophene (T₃) yielded thienyl-terminated Si surfaces. XP survey spectra of these surfaces showed only Si, S, C, and O peaks, with no detectable Li or Br/Cl signals. The position of the S2s signal from the derivatized surface was found to be virtually the same for all thiophene derivatives having a binding energy of 228.6 eV: almost identical to that from free molecules,³ suggesting that the chemical structure of the thienyl rings is retained upon attachment to the surface. The C/Si and S/Si ratios in the XPS measurements increased monotonically with increasing number of thienyl units. It is expected that such attachment is between the surface Si atoms and the α -C of the thienyl rings. Estimation of the organic layer thickness, based on the attenuation of the Si signals arising from the Si(111)-H and thiophene-terminated Si surface was consistent with monolayer thickness of the thiophenes.⁴ Control experiments with non-lithiated thiophenes did not lead to surfaces with detectable amounts of sulfur, establishing the importance of the reactive lithiated reagents in the functionalization of the Si-Br/Cl surface.

Auger spectra of the T and T₃ modified surfaces are shown in Fig. 3. Using sensitivity factors appropriate for a 3 keV beam energy [26] the relative C to S surface coverage for the T and T₃ samples were found to be 4.0 and 5.1, respectively, in reasonable agreement with the relative abundance in the thiophene ring (4.0). The

³ Unpublished data. The S2p binding energy for thiophenes is near 164 eV which overlaps with one of the plasmon peaks of the substrate Si.

⁴ The thickness of thienyl films was estimated from the attenuation of the Si 2p peak intensities, expressed as $I = I_0 \exp(-d/\lambda \sin \theta)$, with I_0 the intensity of the Si 2p on the H-terminated surface, d the film thickness, λ the escape depth of photoelectrons taking as 40 ± 5 Å [3,25], $\theta = 90^\circ$ (the take-off angle of detector on the surface normal). For example, the film thickness for terthiophene-terminated Si surface was estimated to be 14.5 ± 1.8 Å, based on the experimental value $I/I_0 = 0.70$ (Fig. 2a,c). As dimension of Si(111)-T along its long axis is about 12.5 Å, the terthiophene adlayer is within the monolayer range.

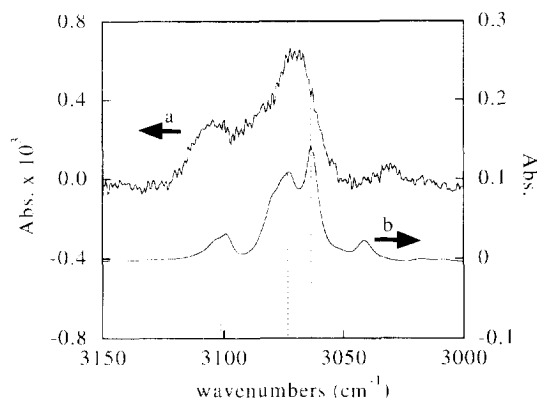


Fig. 4. ATR-FTIR spectra of (a) Si(111)-T₃ prepared by reaction of lithiated terthiophene with Si(111)-Br and (b) polycrystalline T₃ deposited on a freshly oxidized Si ATR element by evaporation of a dilute solution of terthiophene in dichloromethane.

higher value in the T₃ samples suggests a small amount of organic contamination. Both samples contain oxygen and small amounts of unreacted chlorine. Some evidence for surface oxide formation also was observed in the high-resolution of Si 2p spectra of the T₃ modified surface (weak signal centered at ~ 103 eV in Fig. 2).

The absolute surface coverage can be estimated by comparing the Auger electron peak intensities with the Si substrate peak intensity. The strength of the Si Auger signal is characterized by the escape depth of 92 eV electrons through Si as well as the escape depth through the overlayer. Since these escape depths are not well known we assume both to be the same and choose a reasonable estimate of 0.6 nm [27]. If it is assumed that the reactions lead to uniform organic layers, the fraction of surface atoms that have reacted with the organic reagent is estimated to have an upper limit of 0.7 ± 0.2 and 0.3 ± 0.1 for T and T₃, respectively. The size of the thiophene molecule precludes reaction with every surface atom (the dangling bond density on the unreconstructed surface is $7.83 \times 10^{14} \text{ cm}^{-2}$). Thus, it is not surprising to find some oxygen (from hydrolysis of Si(111)X, X = Cl or Br) and halogen on these surfaces. The unreacted halogen will eventually hydrolyze to form oxide during the cleaning process. In the case of the reaction with Si(111)Cl, some residual chlorine was observed owing to the lower reactivity of the chlorinated surface towards water compared to the brominated surface.⁵ It has been suggested by Chidsey and coworkers that even alkyl chains are too large to pack in a 1×1 structure on the Si(111) surface and a 2×1 structure was proposed with the remaining sites occupied by Si-OH groups [1,2]. The thienyl group is actually more closely related in structure to phenyl which also has been proposed to form a 2×1 adlayer on Si(111) [4].

XPS and Auger provide only confirmation of the elemental composition of the modified surface and provide little in the way of proof that the thiophene ring structure has remained intact. Reasonable proof that the thiophene molecule is intact comes from ATR-FTIR and NEXAFS spectroscopy. Reactions were carried out as described above on a Si(111) ATR element ($50 \times 10 \times 1 \text{ mm}^3$). The spectrum of the T₃ modified surface in the aromatic C-H stretch region is shown in Fig. 4a. For comparison, the spectrum of T₃ deposited on a clean ATR element by evaporation of a dilute dichloromethane solution is shown in Fig. 4b. The excellent agreement between these two spectra provides convincing evidence that the ring structure of the molecule is intact on the Si(111) surface. Based on a recent reflectance FTIR study of 2-thio-T₃ on gold [28], the peak intensity at 3070 cm^{-1} in our study ($\approx 1 \times 10^{-5} \text{ A/reflection}$) is consistent with the coverage estimated by AES.

⁵ The presence of the Cl peaks indicates incomplete hydrolysis of the unreacted Si(111)-Cl. The estimated coverage of the Cl was 0.08 for the Si(111)-T. This likely underestimates the Cl coverage since we find that the electron beam desorbs Cl from the Cl terminated Si surface.

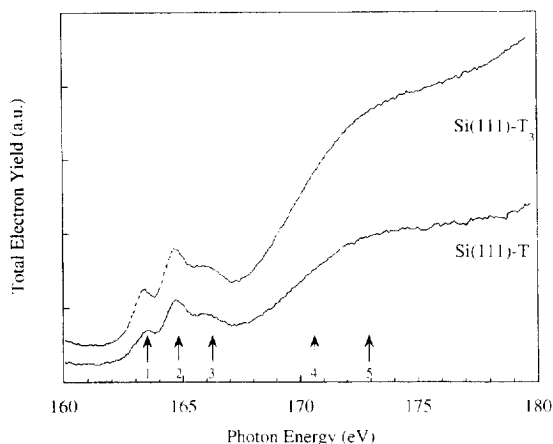


Fig. 5. Sulfur $L_{2,3}$ -edge NEXAFS spectra of 3-methylthiophene (T)- and terthiophene (T_3)-terminated Si(111) surfaces. The background has been subtracted.

Examination of the derivatized Si(111) surface with $SL_{2,3}$ NEXAFS provides further evidence for retention of the thiophene structure on the Si surface. Fig. 5 shows the S $L_{2,3}$ -NEXAFS data from both Si(111)-T and Si(111)- T_3 samples. The intramolecular transitions from S 2p core level to the lowest unoccupied molecular orbitals appear to be the same in both samples, i.e. independent of the number of thienyl units. This is in good agreement with the observation that both thiophene [29] and poly(3-methylthiophene) [30] have the same transitions. The spectra contain peaks assigned to the S $2p_{3/2} \rightarrow \pi^*$ at 163.5 eV (labeled '1' in Fig. 3), to the $2p_{3/2} \rightarrow \sigma^*$ (C-S) and $2p_{1/2} \rightarrow \pi^*$ at 164.7 eV (labeled '2') and to the $2p_{1/2} \rightarrow \sigma^*$ (C-S) at 166.2 eV (labeled '3') transitions, respectively. Transitions attributed to the σ^* (C-C) shape resonance at 170.4 eV (labeled '4') and to the atomic S resonance in the continuum due to excitation to d-like final states at 172.5 eV (labeled '5') are not easily distinguished.

4. Conclusion

We have prepared thiophene-based monolayers covalently bonded to a Si(111) surface using a wet chemical approach. A two-step reaction sequence was employed: bromination or chlorination of Si(111)-H followed by reaction with a lithiated thiophene. This general approach should permit the discrete attachment of thiophene oligomers with longer thienyl units (molecular wires) to Si semiconductor surfaces. We expect that covalent bonding of thiophenes to the Si surface followed by chemical or electrochemical polymerization will improve electron transport between organic layers and the semiconductor. These experiments are in progress.

Acknowledgements

We are grateful to Mr. D. Moffatt for invaluable assistance with FTIR spectroscopic measurements, Mr. R. Dutrisac for technical assistance, Mr. G. Pleizier for recording XPS data, and Dr. D. Klug for valuable discussions.

References

- [1] M.R. Lindford, C.E.D. Chidsey, *J. Am. Chem. Soc.* 115 (1993) 12631.
- [2] M.R. Lindford, P. Fenter, P.M. Eisenberger, C.E.D. Chidsey, *J. Am. Chem. Soc.* 117 (1995) 3145.
- [3] A. Bansal, X. Li, I. Lauermaun, N.S. Lewis, S.I. Yi, W.H. Weinberg, *J. Am. Chem. Soc.* 118 (1996) 7225.
- [4] C. Henry de Villeneuve, J. Pinson, M.C. Bernard, P. Allongue, *J. Phys. Chem. B* 101 (1997) 2415.
- [5] E.J. Lee, J.S. Ha, M.J. Sailor, *J. Am. Chem. Soc.* 117 (1995) 8295.
- [6] E.J. Lee, T.W. Bitner, J.S. Ha, M.J. Shane, M.J. Sailor, *J. Am. Chem. Soc.* 118 (1996) 5375.
- [7] N.Y. Kim, P.E. Laibinis, *J. Am. Chem. Soc.* 119 (1997) 2297.
- [8] K.-H. Li, C. Tsai, J.C. Campbell, M. Kovar, J.M. White, *J. Electron. Mater.* 23 (1994) 409.
- [9] J.A. Glass Jr., E.A. Wovchko, J.T. Yates Jr., *Surf. Sci.* 338 (1995) 125.
- [10] M. Warntjes, C. Vieillard, F. Ozanam, J.-N. Chazalviel, *J. Electrochem. Soc.* 142 (1995) 4138.
- [11] C.W. Sheen, J.X. Shi, J. Martensson, A.N. Parikh, D. Allara, *J. Am. Chem. Soc.* 114 (1992) 1514.
- [12] R.C. Tiberio, H.G. Craighead, M. Lercel, T. Lau, C.W. Sheen, D.L. Allara, *Appl. Phys. Lett.* 62 (1993) 476.
- [13] M. Lercel, G.F. Redinho, H.G. Craighead, C.W. Sheen, D.L. Allara, *Appl. Phys. Lett.* 65 (1994) 974.
- [14] S.R. Lunt, P.G. Santangelo, N.S. Lewis, *J. Vac. Sci. Technol. B* 9 (1991) 2333.
- [15] S.R. Lunt, G.N. Ryba, P.G. Santangelo, N.S. Lewis, *J. Appl. Phys.* 70 (1991) 7449.
- [16] A.M. Spool, K.A. Daube, T.E. Mallouk, J.A. Belmont, M.S. Wrighton, *J. Am. Chem. Soc.* 108 (1986) 3155.
- [17] M. Sturzenegger, N.S. Lewis, *J. Am. Chem. Soc.* 118 (1996) 3045.
- [18] Y. Gu, Z. Lin, R.A. Butera, V.S. Smentkowski, D.H. Waldeck, *Langmuir* 11 (1995) 1849.
- [19] J. Roncali, *Chem. Rev.* 97 (1997) 173.
- [20] G.S. Higashi, Y.J. Chabal, G.W. Trucks, K. Raghavachari, *Appl. Phys. Lett.* 56 (1990) 656.
- [21] K.H. Tan, G.M. Bancroft, L.L. Coatsworth, B.W. Yates, *Can. J. Phys.* 60 (1982) 131.
- [22] J. McMurry, in: *Organic Chemistry* (Brooks/Cole, Monterey, CA, 1984) p. 534.
- [23] L.J. Whitman, S.A. Joyce, J.A. Yarmoif, F.R. Mcfeely, L.J. Terminello, *Surf. Sci.* 232 (1990) 297.
- [24] D.D.M. Wayner, A. Houmam, K.U. Ingold, unpublished results.
- [25] P.E. Laibinis, C.D. Bain, G.M. Whitesides, *J. Phys. Chem.* 95 (1991) 7017.
- [26] L.E. Davis et al., in: *Handbook of Auger Electron Spectroscopy* (Physical Electronics, Eden Prairie, 1976).
- [27] A. Zangwill, in: *Physics at Surfaces* (Cambridge University Press, New York, 1988).
- [28] B. Liedberg, Z. Yang, I. Engquist, M. Wirde, U. Gelius, G. Götz, P. Bäuerle, R.-M. Rummel, Ch. Ziegler, W. Göpel, *J. Phys. Chem. B.* 101 (1997) 5951.
- [29] A.P. Hitchcock, J.A. Horsley, J. Stohr, *J. Chem. Phys.* 85 (1986) 4835.
- [30] G. Tourillon, E. Dartyge, A. Fontaine, R. Garrett, M. Sagurton, P. Xu, G.P. Williams, *Europhys. Lett.* 4 (1987) 1391.