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論文内容の要旨

Carbon based materials are studied intensively due to their interesting electronic and structural properties. They find various applications in nanoelectronics, medicine or material engineering. Those applications where triggered by discovering new carbon materials structures such as fullerens, nanotubes and single graphite sheets so called "graphenes". In nature however carbon element crystal manifests itself in two stable forms - graphite and diamond. They present completely different structural and electronic properties.

Because of strong technological interest graphite-diamond transitions has been studied for a long time. However so far approaches to this problem where mostly concentrated on treating graphite pills with high pressure followed by strong irradiation or high temperature. The method is expensive and the results unsatisfactionary due to a number of impurities. Other method like Chemical Vapor Deposition produces similar difficulties. Recently a new approach has been proposed by so called photo induced phase transition where graphite-diamond transition is induced by a careful light irradiation. The key concept in this idea is multistability where the material possess, besides true ground state, also a false one separated by energy barrier. This barrier is high enough so possible transition through thermal fluctuation is exclude. It is possible however to perform such a transition via photo excitation and lattice relaxation. This process followed by proliferation may end in macroscopic, stable domain resulting new material.

Such a scenario was experimentally induced by Tanimura and Kanazaki. After laser light excitation they observed structural change of graphite sheet. STM images obtained by the group shown a formation of interesting pattern – 1/3 of atoms forming a line along hexagon centers where intruded downwards and 2/3 of atoms where extruded upwards. This suggests forming a new, sp3-type bonds between neighboring layers. What is interesting, transformation was very efficient, less than 10 photon to one, and resulting new material domain has a large size of 1000 atoms order and it is very stable (up to 10 days long). Further investigations revealed that transformation occurs only within two neighbouring layers. Though such transformation is experimentally intriguing it produces many questions and problems. Detailed structure and electronic properties of the new material and transformation mechanism remain a mystery.

Presented Ph.D. thesis present research with following, two goals to achieve:

1. To investigate and find possible ground state diaphite structure. This task includes estimating energy barrier between initial graphite structure and the final one. Furthermore investigating basic properties of new material i.e. size and other geometrical parameters defining it or conditions for stabilization is goal of this project.
2. To postulate and prove process enabling graphite-diaphite transformation.

The structure of the thesis is as follows. Chapter 1 is dedicated to introduction. In Chapter 2 Graphite and Diamond structures will be introduced with detailed explanations of its structural properties. Furthermore crucial concepts of photoinduced phase transitions will be described and its connection to the hypothesis graphite-diamond transition. In Chapter 3 Brenner's potential will be presented as a fundamental tool in our structural calculation. Hence in our calculation we deal with large systems that size is of order 10 000 atoms and more, methods like LDF are no longer possible to use efficiently. Brenner's potential, is member of family of co called bond order potentials and follows the ideas introduced by Abell and Tersoff. Those concepts where successfully imployed in investigations of many carbon based and hydro-carbon based composites. In the thesis the potential was appropriately modified in order to calculate energy barrier between graphite and new phase as well is its geometrical structure. This new material is called by us "diaphite". In the chapter structural calculation using aforementioned potential will be presented. The computations leads to estimation of such a values and properties like energy barrier between phases, structure of the new material, its energetic size evolution or other possible however not optimal candidates for the false ground state. In Chapter 4 possible scenario enabling transformation to occur will be proposed. The chapter introduces the idea of exciton formation due to photoinduced charge transfer between neighboring graphite layer. Most likely electron-hole system will relax due to intralayer conduction. The contents of the chapter however prove that there exist small but finite probability of selflocalization of exciton due to Coulomb's interaction. The Coulomb's interaction triggers graphite net dimerization leading to "diaphite" domain formation. In order to prove this scenario appropriate, minimal Hamiltonian is introduced consisted of electron, phonon and Coulomb interaction part. Using proposed electron-hole-phonon state as a base large scale diagonalization of the Hamiltonian is performed leading to spectrum. Then it is possible to calculate temporal evolution of initial state which leads to finite probability of exciton self localization. In the chapter calculation's details and results will be presented. Finally Chapter 5 will be dedicated to conclusions.

論文の審査結果の要旨

有り触れた"煤"に過ぎないグラファイトから、ダイヤモンドを如何に効率よく合成するかとうい科学技術は、世界中の企業が長年膨大な研究費を費やし、模索してきた問題であり、然も物性物理学上でも極めて大きな純学術的命題でもある。

従来のダイヤモンド合成法は、3000 度、15G パスカルと云う高温高圧下でグラファイトを圧縮する、高エネルギーのガンマ線やX線を強力に照射する等、正に力ずくで、一挙に、強制的にグラファイトをダイヤモンドに変換する方法である。

しかし最近、これらの高温高圧法や衝撃波法を一切用いず、僅かな可視レーザー光照射により、グラファイトからダイヤモンドへ、局所的で、逐次的・量子的、且つ滑らかに相転移させていく方法が、阪大の谷村等によりＳＴＭを用いて実験的に解明・提案され、その理論的真価が問われている。

この状況に鑑み、ラドシンスキー君は、２枚のグラファイト層を対象にして、層間の電荷移動励起に伴うクーロン引力を引き金にして、層間σ結合が逐次的に形成され増殖するとの考えに基づき、この光誘起相転移経路上で予想される種々の過渡的構造の断熱的ポテンシャル面の性質を解明した。10000 個程度の炭素原子を対象にして、ブレナー的半経験論を用い、光励起後の断熱的反応経路を詳細に算出した。

このような多数の原子を、現在汎用されている密度汎函数法で扱う事は事実上不可能であり、現実的な方法ではない。

ラドシンスキー君の、ブレナー理論による計算結果によれば、層内バックリングや層間ズリ変形のように、非平衡相転移の過渡的状態に現れる特殊な結合構造は幾つかあり、同君は、それらの典型的例を逐一、詳細に解明した。この計算により、バリヤーは 1eV 程度であり、炭素原子１００個程からなる準安定なダイヤモンド・ドメインは、グラファイト中で、グラファイト基底状態より 0.5eV 程度上にあるに過ぎないとの結論に達した。

また、光励起後に起きる動力学的過程に関する確率の計算も行い、グラファイトは電気の良導体なので、光電流になって消失・散逸する部分が殆どであるが、３eV の１光子励起当り数%程度は、層間クーロン引力によりσ結合が出来るとの結論も得ている。

この計算結果は、谷村等の実験と良く一致し、世界に先駆けて行なわれた計算でもあり、現在これに比肩する計算は全く見当たらない。

以上の理由から、本論文について審査員全員一致で理学博士の学位に相応しい内容を持つとの結論に至った。