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The Si-doped Zigzag (6,0) AlN Nanotube: A Computational NMR Study

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ABSTRACT

By using of density functional theory (DFT) in theory level of B3LYP and 6-31G(d) basis set, zigzag (6,0) aluminum nitride nanotubes (AlNNTs) structures was investigated in perfect and Si-dope states and for this purpose, NMR parameters involving Chemical Shift Isotropic and Chemical Shift Anisotropic by using GIAO method were investigated. Obtained results were shown that by doping Silicon nucleus on AlN nanotube structure in perfect state, values of NMR parameters were varied for different nucleuses, these variation were depend on position of each nucleus in nanotube structure and chemical medium of nucleus based of neighbor nucleus. However, Si-dope on nanotube structure was caused to changing of regular process for bond angle and bond lengths that existed in perfect state.

Key words: NMR, DFT, AIN Nanotube, Si-dope.

INTRODUCTION

Silicon elements are in IV groups in periodic table that are similar to properties of carbon and Germanium elements. So, these compounds can be used instead of carbon and Germanium elements[1]. But investigating of properties of these compounds as doping nucleus in nanotubes instead of some elements like Carbon and germanium or III and IV groups in periodic table is investigated[2,9,10-12]. Till 1980, three carbon allotrope (none-crystallization carbon) named diamond, graphite and amorphous carbon were discovered, first carbon allotrope that discovered in 1985, was Buckminsterfullerene that however named Buckyball and fullerene[13]. Fullerenes are spherical molecules of carbon that are interesting because of their wonderful properties and beautiful shape[10]. In 1991, other carbon structure was discovered by Sumio Iijima accidently that had unique properties[14]. Iijimia worked in a laboratory in NEC Company in Japan as a electronic microscope expert. When he used transition electronic microscope for observation of fumy products, accidently, observed carbon nanotubes that attached to carbon graphite cathode[1]. At first, he imaged it as a fullerene that

drew in a direction. But finally he noticed that this structure was different from fullerene and because of it, it was named carbon nanotube. In carbon nanotubes, carbon atoms are arranged in cylindrical structures[14]. It means that it's carbonic. Nanotubes are annular compound that in general are single-wall and multi-wall. Van der Waals force is made between multi-wall nanotube. However single-wall models of these compounds in various models are in zigzag, chiral and armchair models. These more applicable nanotubes are involving C-C nanotubes, B-N nanotubes and Al-N nanotubes[2,9]. Al-N nanotubes are more applicable that is because of different physical, chemical properties and electrostatic forces between Al and N nucleuses. In these last years, many studies are done about this compound theoretically and experimentally[16-17]. In fact, researchers want to find new way that by changing of structural properties of these compounds, electrical conductivity, thermal conductivity and application of this compound as Nano-Drug Carriers (NDCs) and as compounds with unique chemical properties can be changed. So, investigating of NMR values parameters can be used in investigating of these compounds. Investigating of NMR parameter gives some information about chemical shift of various nucleus and chemical field around of nucleuses. In fact, investigation of these parameters is done by investigating of chemical shift isotropic (CS^I) and chemical shift anisotropic (CS^A). In 2008, studies were done about Al-N nanotube by Mirzaei et al and investigated doping effects of Carbon nucleus on structure of these compounds[16]. However in 2009, similar studies were done by Farahani et al about these compounds, different states of Al-N nanotubes and B-N nanotubes were compared[14]. But in this study, in a new way, effect of Silicon group are investigated on NMR parameter of Al-N nanotube structure in zigzag (6,0) state.

Computational Methods

By using density functional theory (DFT) in theory level of B3LYP and 6-31G(d) basis set, structure of Al-N nanotube with 10 Angstrom length in zigzag (6,0) model, Si-dope and perfect states was investigated. At first, Al-N nanotube structure was designed in perfect and Si-dope states and nuclear magnetic resonance (NMR) parameter values for these structures were investigated. For this purpose, Chemical Shift Isotropic (CS^I) and Chemical Shift Anisotropic (CS^A) values of these structures were calculated and quality of these changing was considered[15-17]. That following equations were used for investigating of these parameters. Chemical shift tensors in the principal axes system (PAS) ($\sigma 33 > \sigma 22 > \sigma 11$) calculated by mechanic quantum calculation.

$$CS^I\ (ppm) = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3 \quad ...(1)$$

$$CS^A\ (ppm) = \sigma_{33} - (\sigma_{11} + \sigma_{22})/2 \quad ...(2)$$

All calculation was done in Gas phase, 1atm pressure and 298 K temperature and used Gaussian 09w program of package[18]. In general, all calculations were done by Pentium IV PC by intel® processor 1.73 GHz, core i7 and 4 GB of memory in XP® operating system. At first Al-N nanotube structure in zigzag (6,0) model was optimized by AM1 method and finally optimized by DFT method. Molecular formula of Al-N nanotube is $Al_{24}H_{12}N_{24}$ in perfect state and is $Al_{21}\ H_{12}N_{21}Si_6$ in Silicon dope state. In this state, 6 Silicon atoms are doped on Al-N nanotube structure.

RESULTS AND DISCUSSION

At first structures of Al-N nanotube in zigzag (6,0) model in perfect (Fig 1) and Si-dope states (Fig 2) are optimized by theoretical methods. All obtained results are reported in table 1 to 3, involving results of structural parameter, CS^A and CS^I values in different states of AlN nanotube.

Geometrical parameter

Bond length

Obtained results of bond length and bond angles are reported in Table 1 and 2 respectively. All results are shown that calculated values are changed by addition of Silicon nucleus to AlN nanotube. Investigating of values bond length is shown that it is 1.019 angstrom for N-H in perfect state and variation range is 1.018 to 1.021 Å in Si-dope state. But bond length value in Al-H is 1.582 Å in perfect state and it's varied between 1.577 to 1.586 Å in Si-dope state. Investigating of bond length of Al-N is shown that it's not varied in perfect state and its variation range is between 1.807 to 1.818 Å. However, in Si-dope state, variation range is increased and it's because of addition of Silicon

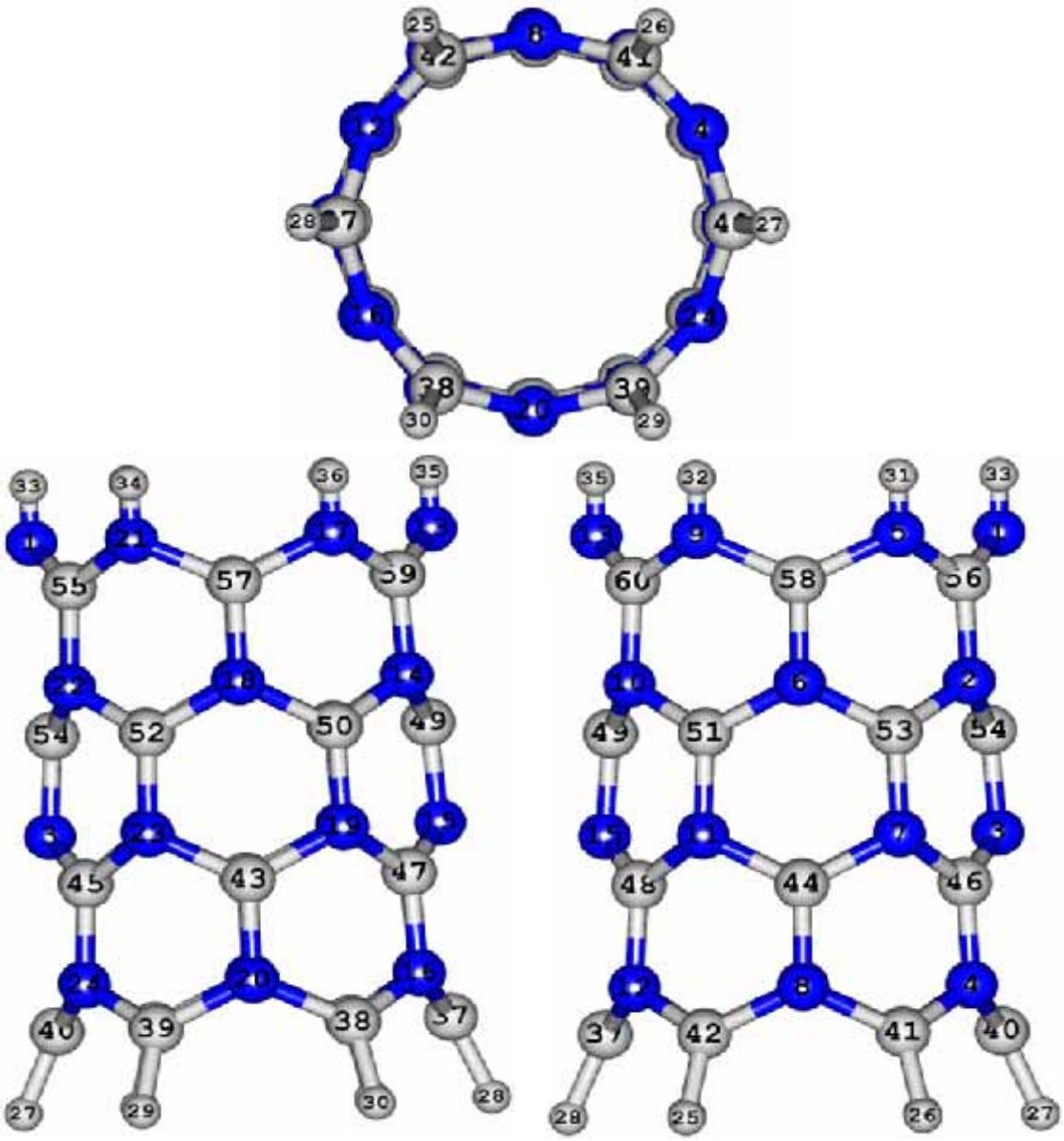

Fig 1. 2D views of the perfect (6,0) AlNNTs.

nucleus. Minimum amount is 1.807 Å in perfect state and maximum amount is 1.818 Å that is smaller in similar bonds. Minimum amount for bond length of Al-N in N11-Al53 for Si-dope state is 1.800 Å and maximum amount is in N8-Al45 and its 1.860 Å. But other bond length are in range of 2.414 to 2.386 Å that is because of increasing of atomic radius. Variation range of Si-Si is between 2.303 to 2.386 Å.

Bond angle

Obtained results are shown that by doping of Si-nucleus instead of bond length and bond angle in AlN nanotubes are changed that it's because of variation of atomic radius. For investigating of bond angles in AlN nanotube, 6 member rings is considered between nanotube in perfect state and different bond angle is considered that is reported in Table 2. These results are shown

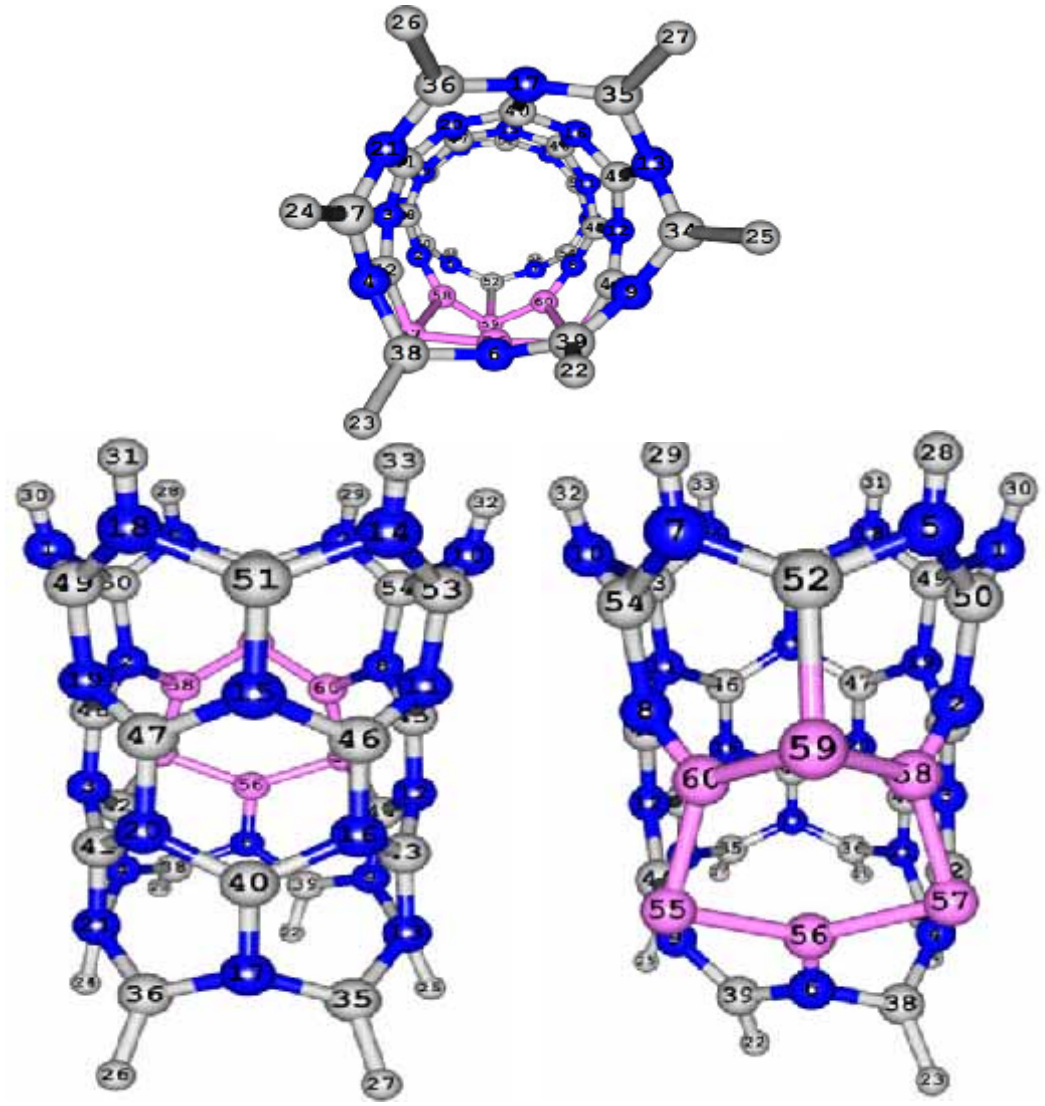

Fig 2. 2D views of the ^{14}Si-dope (6,0) AlNNTs.

that values of bond angle are similar in same state and is in range of 111.3 to 119.3 degree. But by addition of Silicon nucleus on ring, values of bond angle is varied so much that in ring involving Silicon is varied between 83.9 to 133.6 degree, meanwhile external angles of ring is in range of 88.5 to 124.1 degree. However rings without Silicon nucleus, variation is small in perfect state.

NMR properties

For calculation of NMR parameters, at first all structures are optimized and after that NMR parameters of these structures are considered by GAIO method. For this purpose, chemical shift isotropic and chemical shift anisotropic are considered in different state of structures (Fig 1-2).

CS^{I} in zigzag (6,0) AlNNTs in perfect and Si-dope states

Obtained results of CS^{I} are shown that electron density values of nucleus aren't changed and its values are restricted to 221, 183, 173 and 137 ppm. But comparison of this state in Si-dope state is shown that these values are changed by additional of Silicon nucleuses and range of these variations are between 83.13 to 221.36 ppm for Nitrogen nucleuses. However investigation of

Aluminum nucleuses are demonstrated these results. CS^I value for Aluminum nucleus is in range of 437, 450 and 454 ppm in perfect state and in Si-dope state for Al44 nucleus, CS^I value has minimum amount and it is 417.09 ppm. However, in Al48 maximum amount of CS^A is 467.73 ppm. For Silicon nucleus, obtained results are proportional to position of Silicon nucleus into nanotube directly (Table 3) . Maybe CS^I value is considered as shielding or de-shielding of nucleus. Si58, Si60,

Table 1: Bond length (Angstrom) in perfect and Si-dope (6,0) zigzag AlNNTs.

Zigzag (6,0) AlNNTs Si-Dope Bond length				Zigzag (6,0) AlNNTs Perfect Bond length			
N1- H30	1.019	N14- H33	1.018	N1- H33	1.019	N14- Al49	1.816
N1- Al49	1.808	N14- Al51	1.819	N1- Al55	1.815	N14- Al50	1.816
N1- Al50	1.815	N14- Al53	1.814	N1- Al56	1.815	N14- Al59	1.807
N2- Al48	1.866	N15- Al46	1.813	N2- Al53	1.816	N15- Al47	1.815
N2- Al50	1.850	N15- Al47	1.813	N2- Al54	1.816	N15- Al48	1.815
N2- Si58	1.743	N15- Al51	1.804	N2- Al56	1.807	N15- Al49	1.811
N3- Al41	1.824	N16- Al40	1.813	N3- Al45	1.815	N16- Al37	1.818
N3- Al42	1.816	N16- Al43	1.813	N3- Al46	1.815	N16- Al38	1.818
N3- Al48	1.809	N16- Al46	1.802	N3- Al54	1.811	N16- Al47	1.814
N4- Al37	1.804	N17- Al35	1.818	N4- Al40	1.818	N17- H36	1.019
N4- Al38	1.811	N17- Al36	1.816	N4- Al41	1.818	N17- Al57	1.815
N4- Al42	1.823	N17- Al40	1.809	N4- Al46	1.814	N17- Al59	1.815
N5- H28	1.021	N18- H31	1.018	N5- H31	1.019	N18- Al50	1.816
N5- Al50	1.806	N18- Al49	1.814	N5- Al56	1.815	N18- Al52	1.816
N5- Al52	1.817	N18- Al51	1.818	N5- Al58	1.815	N18- Al57	1.807
N6- Al38	1.864	N19- Al47	1.812	N6- Al51	1.816	N19- Al43	1.815
N6- Al39	1.830	N19- Al48	1.810	N6- Al53	1.816	N19- Al47	1.815
N6- Si56	1.733	N19- Al49	1.800	N6- Al58	1.807	N19- Al50	1.811
N7- H29	1.021	N20- Al40	1.813	N7- Al44	1.815	N20- Al38	1.818
N7- Al52	1.817	N20- Al41	1.813	N7- Al46	1.815	N20- Al39	1.818
N7- Al54	1.806	N20- Al47	1.803	N7- Al53	1.811	N20- Al43	1.814
N8- Al45	1.866	N21- Al36	1.823	N8- Al41	1.818	N21- H34	1.019
N8- Al54	1.850	N21- Al37	1.813	N8- Al42	1.818	N21- Al55	1.815
N8- Si60	1.743	N21- Al41	1.815	N8- Al44	1.814	N21- Al57	1.815
N9- Al34	1.817	H22- Al39	1.586	N9- H32	1.019	N22- Al52	1.816
N9- Al39	1.795	H23- Al38	1.577	N9- Al58	1.815	N22- Al54	1.816
N9- Al44	1.827	H24- Al37	1.584	N9- Al60	1.815	N22- Al55	1.807
N10- H32	1.019	H25- Al34	1.582	N10- Al49	1.816	N23- Al43	1.815
N10- Al53	1.807	H26- Al36	1.581	N10- Al51	1.816	N23- Al45	1.815
N10- Al54	1.815	H27- Al35	1.582	N10- Al60	1.807	N23- Al52	1.811
N11- Al45	1.811	Al42- Si57	2.414	N11- Al44	1.815	N24- Al39	1.818
N11- Al46	1.812	Al44- Si55	2.403	N11- Al48	1.815	N24- Al40	1.818
N11- Al53	1.800	Al52- Si59	2.386	N11- Al51	1.811	N24- Al45	1.814
N12- Al43	1.825	Si55- Si56	2.326	N12- Al37	1.818	H25- Al42	1.582
N12- Al44	1.822	Si55- Si60	2.311	N12- Al42	1.818	H26- Al41	1.582
N12- Al45	1.811	Si56- Si57	2.334	N12- Al48	1.814	H27- Al40	1.582
N13- Al34	1.809	Si57- Si58	2.303	N13- H35	1.019	H28- Al37	1.582
N13-Al35	1.823	Si58- Si59	2.325	N13- Al59	1.815	H29- Al39	1.582
N13- Al43	1.815	Si59- Si60	2.325	N13- Al60	1.815	H30- Al38	1.582

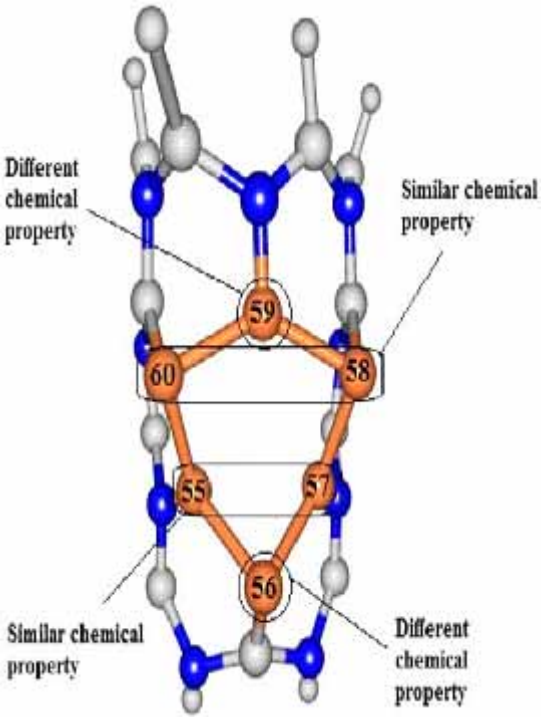

Fig 3. Display classify chemical property in ^{14}Si nucleus.

Si57 and Si55 are equal in some chemical property and Si59 and Si56 have different chemical property (Fig 3).

CS^A in zigzag (6, 0) AlNNTs in perfect and Si-dope states

Obtained results for CS^A values are similar to CS^I results and usually CS^A values are smaller than CS^I. It can be said that by increasing of CS^A and CS^I values are decreased, on the contrary. Value of this parameter for Nitrogen and Aluminum nucleuses are similar in perfect state, so, for Nitrogen nucleus, CS^A values are divided to 27, 28, 30 and 67 ppm. However, for Aluminum nucleuses are 9, 28, 34 and 36 ppm in four different chemical fields. But by doping of Silicon atoms on structure, these variations are increased and based on position of each nucleus to neighbor nucleuses, these variations are complicated. Minimum amount of CS^A for nitrogen is 27.90 ppm in N20 and maximum amount of CS^A for N6 is 217.82 ppm. However, this series is varied for Aluminum nucleuses and for Al36, minimum amount of CS^A is 11.39 ppm and for Al38 nucleuses, maximum

Table 2: Bond angle (Degree) in perfect and Si-dope (6,0) zigzag AlNNTs.

Zigzag (6,0) AlNNTs Si-Dope		Zigzag (6,0) AlNNTs Perfect	
Bond angle		Bond angle	
N6-Si56-Si55	114.9	N10-Al49-N15	119.3
N6-Si56-Si57	111.4	N10-Al49-N14	118.7
Al44-Si55-Si60	98.0	Al48-N15-Al49	117.5
Al44-Si55-Si56	88.5	Al48-N15-Al47	111.3
N8-Si60-Si55	119.3	N16-Al47-N15	119.3
N8-Si60-Si59	124.0	N16-Al47-N19	119.3
Al52-Si59-Si60	96.4	Al43-N19-Al47	111.3
Al52-Si59-Si58	96.3	Al43-N19-Al50	111.3
N2-Si58-Si59	124.1	N18-Al50-N19	119.3
N2-Si58-Si57	119.7	N18-Al50-N14	118.7
Al42-Si57-Si58	97.8	Al59-N14-N50	117.8
Al42-Si57-Si56	88.9	Al59-N14-N49	117.8
Si57-Si58-Si59	115.4	Al49-N15-Al47	117.5
Si58-Si59-Si60	83.9	N15-Al47-N19	119.2
Si59-Si60-Si55	115.6	Al47-N19-Al50	117.5
Si60-Si55-Si56	94.6	N19-Al50-N14	119.3
Si55-Si56-Si57	133.6	Al50-N14-Al49	112.4
Si56-Si57-Si58	94.9	N14-Al49-N15	119.3

Table 3: Isotropic Chemical Shift (ppm) and Anisotropic Chemical Shift (ppm) values for perfect and Si-dope (6,0) zigzag AlNNTs

Zigzag (6,0) AlNNTs					
Perfect			Si-Dope		
Nucleus Symbol & No.	CS^I	CS^A	Nucleus Symbol & No.	CS^I	CS^A
N1	221.23	30.27	N1	218.79	29.58
N2	183.63	28.82	N2	84.16	132.78
N3	173.32	27.71	N3	155.12	47.45
N4	137.58	67.26	N4	116.56	91.20
N5	221.44	28.42	N5	185.50	52.38
N6	183.28	30.43	N6	87.24	217.82
N7	173.94	26.84	N7	185.33	52.40
N8	137.18	67.86	N8	83.13	142.23
N9	221.44	28.42	N9	120.30	90.51
N10	183.63	28.82	N10	218.38	30.62
N11	173.94	26.84	N11	183.77	36.31
N12	137.58	67.26	N12	150.31	49.33
N13	221.23	30.27	N13	130.06	74.94
N14	183.63	28.82	N14	221.10	28.48
N15	173.32	27.71	N15	179.48	36.72
N16	137.58	67.26	N16	170.96	30.69
N17	221.44	28.42	N17	135.78	65.59
N18	183.28	30.43	N18	221.36	28.38
N19	173.94	26.84	N19	183.97	35.67
N20	137.18	67.86	N20	172.08	27.90
N21	221.44	28.42	N21	137.76	66.70
N22	183.63	28.82	Al34	436.75	22.29
N23	173.94	26.84	Al35	436.88	14.29
N24	137.58	67.26	Al36	436.44	11.39
Al37	437.37	9.08	Al37	447.87	19.67
Al38	437.52	9.08	Al38	443.70	80.42
Al39	437.52	9.08	Al39	451.32	60.10
Al40	437.37	9.08	Al40	450.64	30.03
Al41	437.52	9.08	Al41	458.21	29.87
Al42	437.52	9.08	Al42	421.36	32.54
Al43	454.53	28.30	Al43	458.46	29.52
Al44	454.53	28.30	Al44	417.09	50.69
Al45	454.40	28.19	Al45	466.40	75.12
Al46	454.40	28.19	Al46	451.11	39.55
Al47	454.40	28.19	Al47	451.76	39.91
Al48	454.40	28.19	Al48	467.73	74.27
Al49	454.54	36.33	Al49	451.26	28.45
Al50	454.01	36.68	Al50	453.85	49.89
Al51	454.01	36.68	Al51	452.98	37.50
Al52	454.01	36.68	Al52	413.05	35.99
Al53	454.01	36.68	Al53	451.09	27.94
Al54	454.54	36.33	Al54	453.76	50.11
Al55	450.48	34.89	Si55	437.28	138.16
Al56	450.48	34.89	Si56	102.58	453.98
Al57	450.67	35.40	Si57	435.90	128.50
Al58	450.67	35.40	Si58	31.22	397.57
Al59	450.48	34.89	Si59	405.91	187.38
Al60	450.48	34.89	Si60	17.55	415.16

amount is 80.42 ppm. For Nitrogen nucleus, obtained results are similar to results of CS^I state completely (Table 3).

CONCLUSION

After theoretical studies in level of theory B3LYP/6-31G(d) on AlN nanotube zigzag (6,0) model in perfect and Si-dope states, obtained results are stated as following:

- Values of CS^A, CS^I, bond lengths and bond angles in perfect state are regular for AlN nanotube structure that is varied by doping of Silicon on nanotube structure and specific value exists for each parameter based on position of Nitrogen, Aluminum and Silicon nucleuses.
- CS^A and CS^I values it's based on shielded and de-shielded of chemical fields around nucleuses, that in most nucleuses, CS^I value is higher than CS^A value.
- Variation of CS^I value for various nucleuses in perfect state, is Aluminum> Nitrogen> Hydrogen and CS^A value in ^{13}Al, ^{1}H, ^{7}N nucleuses is close to each other. But by addition of Silicon nucleuses to AlN nanotube, this order is changed, and based on kind of nucleuses. Position of each nucleus in different chemical field, proportional neighbor nucleuses, CS^A and CS^I have different value.
- By addition of Silicon nucleus to annular structure of AlN nanotube, because of variation of atomic, ionic radius, bond length is varied and because regular series of AlN nanotube structure is changed, so angle bond is varied too.
- Change of CS^A and CS^I value is effected on thermal conductivity and electrical conductivity properties that quality of these variations should be considered in future.

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