

Thermodynamic analysis of tetrahedral carbon hybridization in sputtered amorphous carbon films deposited without energetic ion bombardment

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Abstract

A thermodynamic analysis of tetrahedral carbon hybridization (sp^3) in sputtered amorphous carbon (a-C) thin films is presented for low-pressure radio-frequency (rf) plasma discharges in the absence of energetic ion bombardment. The model is based on the fact that sp^3 hybridization in these rf sputtered a-C films is an intrinsic spontaneous process governed by thermodynamic first principles that occurs without the assistance of an external agent. The analysis shows that the sp^3 atomic concentration depends on the compressive (hydrostatic) stress arising at sp^3 -bonded carbon atom sites and the degree of film densification. Good agreement is found between analytical and experimental results for the sp^3 content of a-C films deposited at room temperature without Ar^+ bombardment. The present thermodynamic analysis explains why the residual stress in rf sputtered a-C films cannot be directly related to the sp^3 content and why post annealing of dense a-C films synthesized with the assist of ion bombardment should not significantly affect the sp^3 content.

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Since the discovery of the trigonal (graphite-like) and tetragonal (diamond-like) atomic carbon hybridizations in amorphous carbon (a-C) films (sp^2 and sp^3 , respectively) and the proposed three-dimensional carbon network structure,¹ significant effort has been devoted to the study of the effect of deposition conditions on the formation of these allotropic carbon phases. The sp^3 hybridization in nonhydrogenated tetrahedral a-C films due to the bombardment of energetic carbon ions is a physical process that can be explained by the subplantation model.²⁻⁶ The sp^3 content in a-C films produced from low-pressure radio-frequency (rf) plasma discharges can be as high as ~50 at.% when an optimum negative bias voltage is applied to the substrate during sputtering. Although energetic particle bombardment on the growing film surface is believed to be essential for the synthesis of nonhydrogenated a-C films rich in sp^3 hybridization, sp^3 contents of the order of ~30 at.% can be found in sputtered a-C films deposited without ion bombardment. Since low-energy (~10 eV) neutral carbon atoms are film precursors in rf sputtering, the effect of energetic particle bombardment on sp^3 hybridization is secondary and the formation of sp^3 carbon configurations is a spontaneous process. The mechanism of sp^3 hybridization in these a-C films differs significantly from those encountered in carbon films produced under conditions involving energetic ion bombardment.

In sputtered a-C films deposited without ion bombardment, sp^3 carbon atoms are in a state of thermodynamic equilibrium. Therefore, minimization of the appropriate thermodynamic energy function controls sp^3 hybridization. Hence, the objective of this study was to derive a thermodynamic analysis of sp^3 hybridization in sputtered a-C films deposited in the absence of ion bombardment and to demonstrate its validity through comparisons with experimental measurements.

According to the second law of thermodynamics, a system is at a state of thermodynamic equilibrium if and only if the Gibbs free energy of the system,

$$G = U + PV - TS, \quad (1)$$

where U is the internal energy, P is the pressure, V is the volume, T is the temperature, and S is the entropy, reaches a minimum. Consider the sputtering of an a-C film without energetic ion bombardment where N_1 and N_2 carbon atoms exist at the growing film surface in sp^3 and sp^2 hybridizations, respectively. Then, the total mole number of carbon atoms n is given by

$$n = \frac{N_1 + N_2}{N_A}, \quad (2)$$

where N_A is the Avogadro constant (6.023×10^{23} atoms/mole), and the atomic concentration of sp^3 hybridization is obtained as

$$x = \frac{N_1}{nN_A}. \quad (3)$$

Since each carbon atom can form four single bonds with four other neighboring atoms, the average number of bonds per carbon atom is equal to 4/5, and the internal energy U can be expressed as

$$U = \frac{4}{5} e(N_1 \mathbf{e}_{sp^3} + N_2 \mathbf{e}_{sp^2}) = \frac{4}{5} nN_A e [x \mathbf{e}_{sp^3} + (1-x) \mathbf{e}_{sp^2}], \quad (4)$$

where \mathbf{e}_{sp^3} (= 3.70 eV) and \mathbf{e}_{sp^2} (= 3.91 eV) are the strengths of sp^3 and sp^2 carbon bonds,⁷ respectively, e (= 1.602×10^{-19} C) is the elemental charge, and U is expressed in Joules.

The term PV in Eq. (1) can be expressed as

$$PV = P_{sp^2} V_{sp^2} + P_{sp^3} V_{sp^3}, \quad (5)$$

where P_{sp^2} and P_{sp^3} are the atomic pressures at sp^2 and sp^3 carbon bonding sites, respectively, and V_{sp^2} and V_{sp^3} are the corresponding volumes occupied. Since the sp^3 hybridized carbon atoms are at a state of thermodynamic equilibrium, the atomic pressure at sp^3 carbon sites P_{sp^3} can be set equal to the thermodynamic equilibrium pressure of diamond P_{diam} at a temperature T , given in the pressure-temperature phase diagram of carbon. Because $P_{diam} \approx 1.5$ GPa at 298 K,⁸ it may be inferred that at 298 K, $P_{sp^3} = P_{diam} \approx 1.5$ GPa.

A common feature in a-C films is the presence of a compressive equibiaxial stress. Considering that the pressures at sp^2 and sp^3 carbon sites represent hydrostatic stresses, the localized (atomic) stresses are $\mathbf{s}_{sp^2} = \frac{3}{2}P_{sp^2}$ and $\mathbf{s}_{sp^3} = \frac{3}{2}P_{sp^3}$, respectively. Hence, the average residual stress \mathbf{s}_{res} can be written in terms of the localized stresses and sp^3 carbon content as

$$\mathbf{s}_{res} = (1-x)\mathbf{s}_{sp^2} + x\mathbf{s}_{sp^3} = \frac{3}{2}[(1-x)P_{sp^2} + xP_{sp^3}]. \quad (6)$$

For sputtered a-C films with ~30 at.% sp^3 deposited at room temperature and under the assumption that $P_{sp^2} = 0$, Eq. (6) gives $\mathbf{s}_{res} = 1.5xP_{sp^3} \approx 0.675$ GPa.

To verify the validity of the above assumptions, the average residual stress in two a-C films was determined using the curvature method. The films were synthesized by Ar⁺ sputtering of a pure graphite target in a rf sputtering system without magnetron (Perkin-Elmer Randex-240) under forwarded rf power of 200 and 750 W without biasing the substrate. The wafer thickness t_s was measured with a probe instrument (Millitron), while the wafer radius of curvature was evaluated before and after film deposition by laser scanning (Flexus). The film thickness t_f was determined directly from high-resolution cross-section transmission electron microscopy (Philip

CM-300) images obtained at different locations of the same film sample. The average residual stress in the films was determined using Stoney's relationship⁹

$$\mathbf{s}_{res} = \left(\frac{E}{1-\mathbf{n}} \right)_s \frac{t_s^2}{6t_f} \left(\frac{1}{r} - \frac{1}{r_o} \right), \quad (7)$$

where $(E/1 - \mathbf{n})_s$ is the biaxial modulus of the Si(100) substrate (assumed equal to 180.5 GPa¹⁰), and r_o and r are the radii of curvature of the Si(100) substrate measured before and after film deposition, respectively. The residual compressive stress corresponding to 200 and 750 W rf power was found to be equal to 0.83 and 0.75 GPa, respectively, i.e., close to the value of 0.675 GPa predicted from the analysis, confirming that the above assumptions are justifiable. Thus, the term PV can be written as

$$PV = P_{sp^3} V_{sp^3} = P_{diam} V_{sp^3}. \quad (8)$$

The volume occupied by sp^3 carbon atoms is given by

$$V_{sp^3} = N_1 V_{sp^3-C} = xnN_A V_{sp^3-C}, \quad (9)$$

where V_{sp^3-C} is the average volume occupied by an sp^3 -bonded carbon atom. In diamond, the average volume occupied by a carbon atom is equal to $\sim \frac{4}{3} \mathbf{p}r_{sp^3}^3$, where r_{sp^3} ($= 0.154$ nm) is the length of an sp^3 bond.¹¹ Since the sp^3 -bonded carbon atoms in an a-C film are less constrained than those in diamond, it follows that $V_{sp^3-C} > \frac{4}{3} \mathbf{p}r_{sp^3}^3$. Hence,

$$V_{sp^3-C} = k \left(\frac{4}{3} \mathbf{p}r_{sp^3}^3 \right), \quad (10)$$

where $k (> 1)$ is a constant. Therefore, PV can be expressed as

$$PV = xnN_A P_{diam} k \left(\frac{4}{3} \mathbf{pr}_{sp^3}^3 \right). \quad (11)$$

The term TS in Eq. (1) is given by

$$TS = nTs = nT(s^o + \Delta s), \quad (12)$$

where $s = s^o + \Delta s$ is the molar entropy, with s^o and Δs representing entropy contributions of atomic vibration, rotation, etc., and structural configuration, respectively. The configuration entropy Δs , given by¹²

$$\Delta s = -R[x \ln x + (1-x) \ln(1-x)], \quad (13)$$

where $R (= 8.31 \text{ J/mol K})$ is the molar gas constant, provides a measure of the degree of disorder in a glassy material and exhibits the greatest effect on the material structure,¹³ i.e., $\Delta s \gg s^o$.

Therefore, $s \approx \Delta s$, and TS can be expressed as

$$TS = -nTR[x \ln x + (1-x) \ln(1-x)]. \quad (14)$$

Substituting Eqs. (4), (11), and (14) in Eq. (1), and dividing by the total mole number n , the Gibbs molar free energy g is obtained as

$$g = \frac{4}{5} N_A e \left[x \mathbf{e}_{sp^3} + (1-x) \mathbf{e}_{sp^2} \right] + \frac{4}{3} k \mathbf{pr}_{sp^3}^3 x N_A P_{diam} + TR[x \ln x + (1-x) \ln(1-x)] \quad (15)$$

At thermodynamic equilibrium, the Gibbs molar free energy assumes a minimum, i.e., $dg/dx = 0$ and $d^2g/dx^2 > 0$. Using Eq. (15),

$$\frac{dg}{dx} = \frac{4}{5} N_A e (\mathbf{e}_{sp^3} - \mathbf{e}_{sp^2}) + \frac{4}{3} k \mathbf{pr}_{sp^3}^3 N_A P_{diam} + TR \ln \left(\frac{x}{1-x} \right), \quad (16)$$

and

$$\frac{d^2g}{dx^2} = \frac{TR}{x(1-x)}. \quad (17)$$

From Eq. (17), $d^2g/dx^2 > 0$ is always satisfied because $0 < x < 1$. Setting $dg/dx = 0$, the atomic concentration of sp^3 at thermodynamic equilibrium is found to be

$$x = \frac{e^b}{1 + e^b}, \quad (18)$$

where

$$b = -\frac{N_A}{TR} \left[\frac{4}{5} e(\mathbf{e}_{sp^3} - \mathbf{e}_{sp^2}) + \frac{4}{3} k \mathbf{pr}_{sp^3}^3 P_{diam} \right]. \quad (19)$$

Since the diamond-to-graphite density ratio is ~ 1.55 and the sp^3 content is assumed to be equal to ~ 30 at.%, k obtains values in the range of 1.3–1.4, and the atomic concentration of sp^3 is predicted from Eqs. (18) and (19) to be between 33 and 22 at.%. Figure 1 shows the variation of g with x for $k = 1.35$. The value of x corresponding to the minimum value of g is equal to 27.2 at%.

To examine the validity of the analytical model, thin a-C films were deposited on Si(100) under conditions of forwarded rf power in the range of 298–755 W, zero substrate bias, 20 sccm Ar gas flow rate, 3 mTorr working pressure, and 3 min deposition time. The substrate temperature was maintained at room temperature by a cooling system. X-ray photoelectron spectroscopy (XPS) studies of the a-C film surfaces were performed with an XPS system (PHI Model 5400). Gaussian-Lorentzian (GL) profiles were fit to the C 1s XPS spectra using a standard least-squares algorithm, after subtracting the background noise based on the Shirley method.

Díaz et al.¹⁴ reported that the line positions of sp^2 and sp^3 hybrids in the C 1s spectrum of a-C films deposited by pulsed laser evaporation of graphite targets are at 284.3 and 285.2 eV, respectively, i.e., 0.9 eV upward shift of the binding energy of sp^3 hybrids with respect to sp^2 hybridized carbon. Jackson et al.¹⁵ reported that the binding energies of 284.84 and 285.8 eV in

a-C films deposited by dc magnetron sputtering and cathodic arc deposition corresponded to sp^2 and sp^3 bonded carbons, respectively. Taki and Takai¹⁶ assigned the sharp peaks at 284.15 and 285.5 eV in the spectra of graphite and diamond, respectively, to the binding energies of sp^2 and sp^3 bonded carbon in hydrogenated a-C films synthesized by shielded arc ion plating and reported that the full-width at half-magnitude (FWHM) values for graphite and diamond are equal to 1.0 and 2.2 eV, respectively. Mérel et al.¹⁷ found that the binding energies of sp^2 and sp^3 hybridized carbon atoms in pulsed laser deposited a-C films are equal to 284.4 and 285.2 eV, respectively, and the corresponding FWHM equal to 1.0 and 1.1 eV. Tay et al.¹⁸ found that the line positions of sp^2 and sp^3 carbon bonding in a-C films deposited by the filtered cathodic vacuum arc technique are at 284.3 and 285.1 eV, respectively, and Lu and Komvopoulos^{19,20} reported that the binding energies of sp^2 and sp^3 hybridized carbon atoms in rf sputtered a-C films are in the ranges of 284.24-284.45 eV and 285.36-285.44 eV, respectively, depending on the deposition conditions.

In view of the results of the above investigations, the search of the sp^2 and sp^3 binding peak positions in the deposited a-C films was performed in the ranges of 283.95-284.55 and 284.95-285.70 eV, respectively, while the sp^1 binding peak position was searched in the range of 282-283.5 eV. To account for the effect of oxygen atoms from the ambient, three additional peaks were searched in the ranges of 286-287, 287-288.5, and 288.5-290.5 eV, respectively.²⁰ Hence, six GL profiles were used to fit the C 1s core level XPS spectra. FWHM values of all the XPS peaks were obtained in the range of 0-3 eV.

Table I gives information about the film deposition conditions and the decomposition of the C1s core level XPS spectra. The sp^3 -bonded carbon atom concentrations in these films are in the range of 26–28 at.%, independent of the rf power. These experimental results are in good

agreement with the prediction of the present thermodynamic model, i.e., 27.2 at.% sp^3 carbon bonding. The favorable comparison of analytical and experimental results confirms that sp^3 carbon hybridization in rf sputtered a-C films deposited without energetic ion bombardment is an intrinsic process controlled by thermodynamics.

Figure 2 shows the atomic concentration of sp^3 carbon hybridization as a function of k [Eq. (10)]. Both the constraint of sp^3 carbon atom configurations and the film density increase as $k \rightarrow 1.0$, resulting in higher sp^3 atomic concentration approaching to 70 at.%. Therefore, \mathbf{g} ($= 1/k$) reflects the degree of densification in the film. Since $P_{sp^3} = P_{diam} = \frac{2}{3}\mathbf{s}_{sp^3}$, Eq. (19) can be rewritten as

$$\mathbf{b} = -\frac{N_A}{TR} \left[\frac{4}{5} e(\mathbf{e}_{sp^3} - \mathbf{e}_{sp^2}) + \frac{8}{9} \mathbf{pr}_{sp^3} \frac{\mathbf{s}_{sp^3}}{\mathbf{g}} \right]. \quad (20)$$

In view of Eqs. (18) and (20), the atomic concentration of sp^3 carbon hybridization is a function of $\mathbf{s}_{sp^3} / \mathbf{g}$, i.e., both the localized (atomic) stress and the degree of film densification determine the sp^3 carbon content. For a-C films with the same compressive atomic stress, the degree of densification depends on the deposition technique, and, thus, the sp^3 carbon content in these films will differ. The residual stress in a-C films with the same sp^3 carbon content also depends on the deposition conditions. Equations (6), (8), and (20) provide justification for the lack of direct correlation between the sp^3 content and the compressive residual stress in ta-C films.²¹

It is well known that energetic ion bombardment produces metastable and dense a-C films characterized by relatively high sp^3 content due to greater film densification than that obtained without ion bombardment. However, the relative high compressive residual stress in these films

often leads to premature delamination and cracking. Therefore, reducing the residual stress by post annealing without affecting significantly the sp^3 content in these films is of great significance. Since annealing does not affect ρ , while it causes the residual stress in the film to decrease to the thermodynamic equilibrium value, high sp^3 contents would be maintained in these films, as shown in Fig. 2 This conclusion is supported by the simulation result of a molecular dynamics study.²²

The present thermodynamic analysis demonstrates that, in the absence of energetic ion bombardment during film growth, sp^3 carbon hybridization in sputtered a-C films is an intrinsic and spontaneous process controlled by thermodynamics. It was shown that sp^3 carbon hybridization depends on both the compressive residual stress and the degree of densification in the a-C films. Experimental results revealed that the sp^3 atomic carbon content in a-C films sputtered at room temperature and without energetic ion bombardment is in the range of 26–28 at.%, regardless of the rf power, which is in good agreement with the analytical prediction (~27.2 at.% sp^3). Moreover, the analysis yields insight into the underlying reason for the lack of direct correlation between the compressive residual stress and the sp^3 content of a-C films and shows that the effect of post annealing of dense a-C films produced by energetic ion bombardment on the sp^3 content is secondary.

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- ¹J. Kakinoki, K. Katada, T. Hanawa, and T. Ino, *Acta Cryst.* **13**, 171 (1960).
- ²Y. Lifshitz, S. R. Kasi, J. W. Rabalais, and W. Eckstein, *Phys. Rev. B* **41**, 10468 (1990).
- ³Y. Lifshitz, S. R. Kasi, and J. W. Rabalais, *Phys. Rev. Lett.* **62**, 1290 (1989).
- ⁴J. Robertson, *Diamond Rel. Mater.* **3**, 361 (1994).
- ⁵J. Robertson, *Diamond Rel. Mater.* **5**, 519 (1996).
- ⁶H. Hofsäss, H. Feldermann, R. Merk, M. Sebastian, and C. Ronning, *Appl. Phys. A* **66**, 153 (1998).
- ⁷H. Efstathiadis, Z. Akkerman, and F. W. Smith, *J. Appl. Phys.* **79**, 2954 (1996).
- ⁸J. C. Angus, Structure and thermochemistry of diamond, in *The Physics of Diamond*, edited by A. Paoletti and A. Tucciarone (IOS Press, Amsterdam, The Netherlands, 1997) pp. 9-30.
- ⁹A. Brenner and S. Senderoff, *J. Res. Natl. Bur.* **42**, 105 (1949).
- ¹⁰W. A. Brantley, *J. Appl. Phys.* **44**, 534 (1973).
- ¹¹W. Kulisch, *Deposition of Diamond-Like Superhard Materials* (Springer-Verlag, Berlin, Germany, 1999) p. 28.
- ¹²D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, 2nd edition (Krieger Publishing, Malabar, Florida, 1987) p. 88.
- ¹³S. M. Allen and E. L. Thomas, *The Structure of Materials* (Wiley, New York, 1999) p. 23.
- ¹⁴J. Díaz, G. Paolicelli, S. Ferrer, and F. Comin, *Phys. Rev. B* **54**, 8064 (1996).
- ¹⁵S. T. Jackson and R. G. Nuzzo, *Appl. Surf. Sci.* **90**, 195 (1995).
- ¹⁶Y. Taki and O. Takai, *Thin Solid Films* **316**, 45 (1998).
- ¹⁷P. Mérel, M. Tabbal, M. Chaker, S. Moisa, and J. Margot, *Appl. Surf. Sci.* **136**, 105 (1998).
- ¹⁸B. K. Tay, X. Shi, H. S. Tan, and D. H. C. Chua, *Surf. Interf. Anal.* **28**, 231 (1999).
- ¹⁹W. Lu and K. Komvopoulos, *J. Appl. Phys.* **85**, 2642 (1999).

²⁰W. Lu and K. Komvopoulos, *J. Appl. Phys.* **89**, 2422 (2001).

²¹A. C. Ferrari, S. E. Rodil, J. Robertson, and W. I. Milne, *Diamond Rel. Mater.* **11**, 994 (2002).

²²P. C. Kelires, *Diamond Rel. Mater.* **10**, 139 (2001).

TABLE I. Deposition conditions, decomposition of C1s core level XPS spectra, and sp^3 carbon atom concentration of rf sputtered a-C films.

Deposition conditions		Decomposition of C1s core level XPS spectra				sp^3
Absorbed rf power (W)	Target bias voltage (V)	Peak Positions (eV)	FWHM (eV)	GL* (%)	Area (%)	(at.%)
298.5	-1095	282.59	1.09	0	0.9	26.7
		284.482	1.598	3	56.6	
		285.62	1.637	7	20.6	
		286.702	1.63	2	8.6	
		288.063	2.424	0	6.2	
		289.031	2.392	64	7.1	
401	-1290	282.611	1.144	0	1.3	27.2
		284.36	1.478	4	59.5	
		285.63	1.73	0	22.2	
		286.95	1.554	0	8.1	
		288.5	1.943	0	5.6	
		289.806	3	0	3.3	
496.5	-1400	282.77	1.06	0	1.1	26.1
		284.39	1.45	10	58.6	
		285.648	1.766	0	20.7	
		286.77	1.668	34	8.8	
		288.1	2.201	1	5.9	
		289.217	3	18	4.9	

TABLE I. Deposition conditions, decomposition of C1s core level XPS spectra, and sp^3 carbon atom concentration of rf sputtered a-C films (cont'd)

Deposition conditions		Decomposition of C1s core level XPS spectra				sp^3
Absorbed rf power (W)	Target bias voltage (V)	Peak Positions (eV)	FWHM (eV)	GL* (%)	Area (%)	(at.%)
595	-1550	282.79	1.186	0	1.5	27.7
		284.35	1.42	8	57.6	
		285.671	2.002	0	22.1	
		286.832	1.724	0	9.2	
		288.462	1.843	0	5.9	
		289.631	2.69	0	3.7	
746.5	-1750	283.273	1.722	0	3.6	26.8
		284.334	1.333	14	56.8	
		285.444	1.967	0	20.8	
		286.785	1.898	7	7.7	
		287.29	2.555	0	3.6	
		288.851	2.33	41	7.5	

*Note: 0% and 100% GL denotes pure Gaussian and pure Lorentzian profile, respectively.

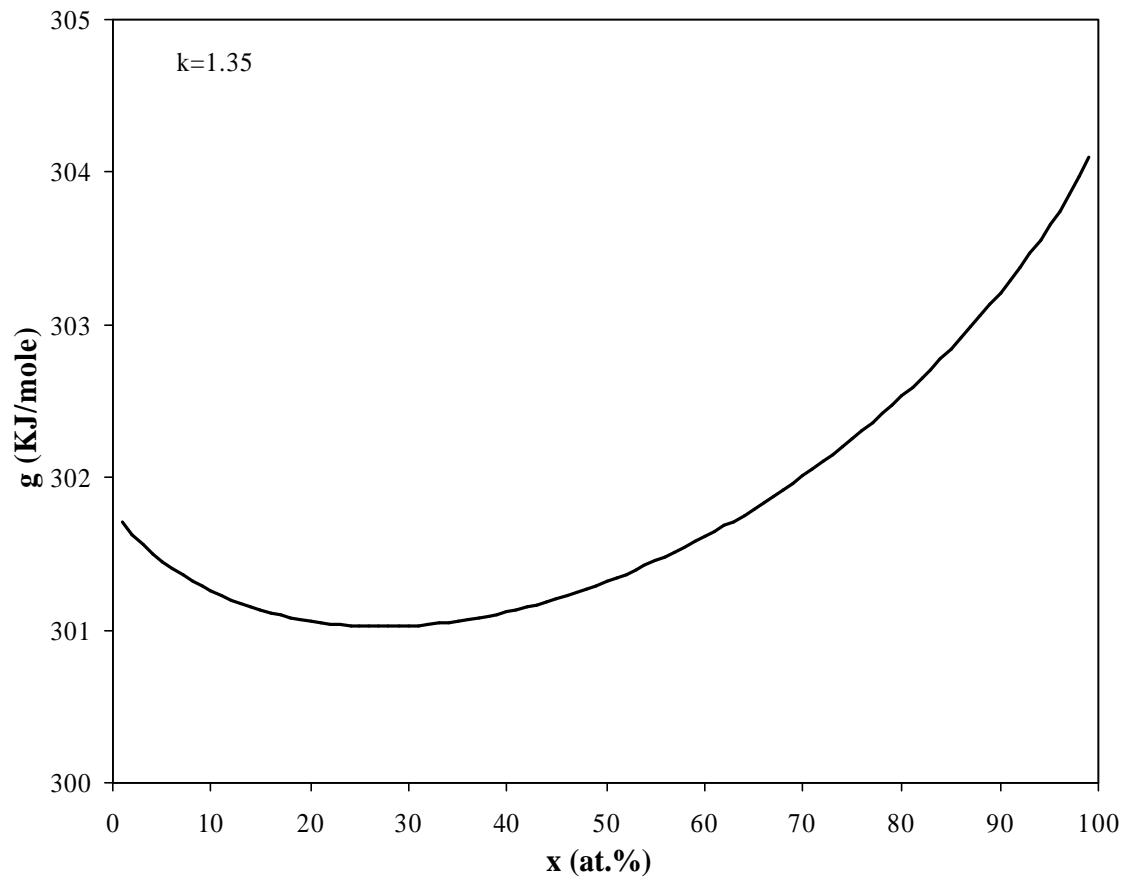


FIG. 1 Gibbs molar free energy versus atomic concentration of sp^3 hybridization in sputtered a-C film for densification parameter $k = 1.35$.

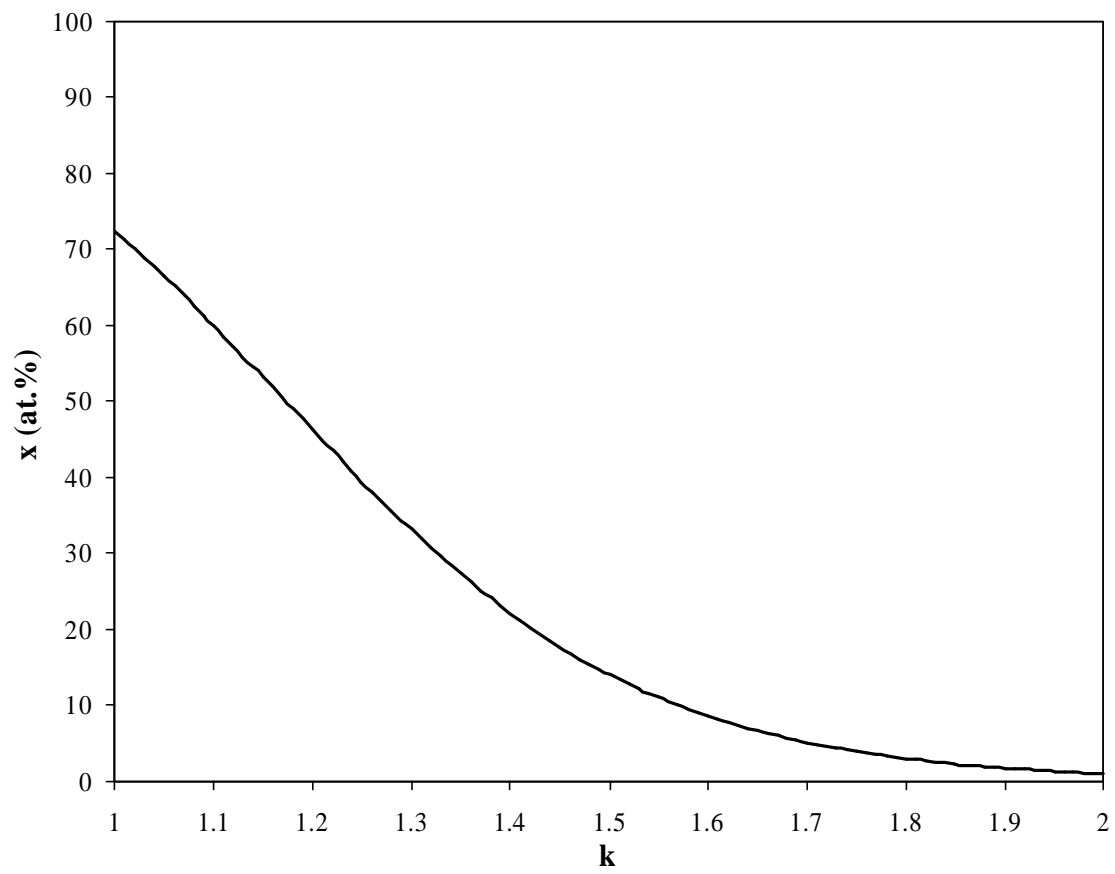


FIG. 2 Atomic concentration of sp^3 hybridization in sputtered a-C films versus densification parameter k .