Thermodynamic analysis of chemical processes in Ni/Cr/Si structure for carbon nanotubes growing by CVD

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Abstract. This paper presents results of the thermodynamic analysis of chemical processes in the Ni/Cr/Si structure during the formation of catalytic centers and the growth of carbon nanotubes on them. It is shown that before starting CVD process Ni/Cr/Si structure is oxidized in atmosphere, and the Cr underlayer oxidation occurs due to an exchange reaction between Cr and NiO, with the formation of chromium oxide. Argon is supplied during the heating displaces residual atmospheric gases, and ammonia due to decomposition under the action of temperature allows to bind the free oxygen in the water vapor. The activation step may be accompanied by a reduction reaction of the oxide of catalyst material up to full reduction of nickel. It was revealed that under nickel CC formed the complex composition underlayer Cr/Cr_xO_y/CrSi_2, which is a diffusion barrier, which prevents the interaction of nickel with a silicon substrate. It is shown that in the growth stage decomposition of acetylene occurs on nickel CC with the release of free carbon, however in the underlayer may be formed a solid solution of Cr_2O_3 and Cr_3C_2.

1. Introduction

Carbon nanotubes (CNTs) are already finding application in various fields of electronic engineering [1-5], and is a promising material for the creation of a new element base of nanoelectronics [6]. The method of chemical vapor deposition (CVD) remains the most promising method [7], due to the possibility of local and controlled growth of CNTs on a pre-formed catalytic centers (CC) [7, 8]. At the same time to create the device structures it is an important condition for the formation of the contact to the base of the CNT. In [9] it is shown that different combinations of materials catalyst/underlayer/substrate results in significantly different parameters of CNTs grown on them. In [9, 10] it is shown that the use of Ni as catalyst and Cr as an underlayer provides a CNT with a better "growth quality". Therefore, carrying out the thermodynamic analysis of the interaction of the materials used as a catalyst (Ni), the underlayer (Cr) and the substrate (Si) at various stages of CC formation and CNT growth, with considering the composition of the process media at all stages of CVD process is an important task.

2. Experimental methodology

Establishing laws of thermodynamic processes in the interfacial interaction of materials in structure Ni (10 nm)/Cr (20 nm)/Si (380 µm) was performed using a commercially available program package FactSage 6.2 (GTT Technologies, Germany). Determination of the temperature dependence of the
change of the Gibbs free energy $\Delta G (T)$ and drawing of phase diagrams was carried out with considering the non-linear thermo-physical properties of materials and real technological modes of CNTs growing. Consideration of the steps of the CVD process for growing CNTs (heating, activation and growth) was performed with the following conditions:

- heating is carried out to a temperature of 1000 °C;
- basic material layers do not act as a diffusion barrier structure by inhibiting the interaction of a component in the system (as a consequence of their nanoscale thickness);
- catalyst material layer may have a native oxide formed by oxidation of a sample of the residual atmosphere in the reaction chamber.

Thermodynamic analysis was conducted by comparing the temperature dependence of the Gibbs free energy change $\Delta G (T)$ of all possible chemical reactions in the system according to the formulas:

$$\Delta H^*_T = \Delta H^*_{298} + \int_{298}^T \Delta C_p (T) dT,$$

$$\Delta S^*_T = \Delta S^*_{298} + \int_{298}^T \frac{\Delta C_p (T)}{T} dT,$$

where $H$ - the enthalpy of the system, $S$ - entropy of the system, $C_p$ – heat capacity of a substance mole, $T$ - temperature of the process.

On heating stage the sample is annealed to the temperature of 600-1000 °C at pressures of 3-5 Torr in Ar and NH$_3$ atmosphere. When loading the sample into the CVD chamber is its contact with air, which can lead to oxidation of metal films, and the oxidation process can occur by three mechanisms:

- Ni and Cr reacting with oxygen from the atmosphere;
- Ni and Cr reacting with water vapor from the atmosphere;
- Cr oxidation by reaction with nickel oxide.

These mechanisms are considered as additional components of the system during the subsequent thermodynamic analysis.

The calculation and analysis of changes in the Gibbs free energy $\Delta G(T)$ were carried out with considering of molar (stoichiometric) ratios of the chemical reactions between substances, but for clarity in the text of the work these ratios are not given.

We considered reactions of the oxidation of Cr and Ni of atmospheric water vapor and oxygen at the beginning of the heating in the CVD chamber at a pressure of 4.5 Torr.

Reactions of Ni with O$_2$ and H$_2$O:

$$\text{Ni} + \text{H}_2\text{O} \rightarrow \text{NiO} + \text{H}_2;$$

$$2\text{Ni} + \text{O}_2 \rightarrow 2\text{NiO}.$$  \hspace{1cm} (3) \hspace{1cm} (4)

Taking into account that in a real sample NiO film can restrict direct access of oxygen or water vapor to the Cr underlayer, it is necessary to consider the Cr oxidation reaction by its contact with the nickel oxide:

$$3\text{NiO} + 2\text{Cr} \rightarrow 3\text{Ni} + \text{Cr}_2\text{O}_3.$$  \hspace{1cm} (5)

The interaction of Cr and oxygen can lead to a number of oxides:

$$2\text{Cr} + \text{O}_2 \rightarrow 2\text{CrO};$$  \hspace{1cm} (6)

$$\text{Cr} + \text{O}_2 \rightarrow \text{CrO}_2;$$  \hspace{1cm} (7)

$$4\text{Cr} + 3\text{O}_2 \rightarrow 2\text{Cr}_2\text{O}_3.$$  \hspace{1cm} (8)

On heating stage in the CVD process the pressure in chamber is maintained at 4.5 Torr, and simultaneously NH$_3$ (15 cm$^3$/min) and Ar (40 cm$^3$/min) fed to the chamber. Taking into consideration
that Ar - inert gas which serves to fill the chamber volume and displacement of the residual atmosphere in the heating process, we can exclude its interaction with components of the structure.

Consider the ammonia decomposition reaction (9) and its decomposition in the presence of residual oxygen from the atmosphere (10, 11), and the direct interaction of oxygen and hydrogen obtained by dissociation of ammonia (12):

\[
\begin{align*}
2\text{NH}_3 &\rightarrow \text{N}_2 + 3\text{H}_2, \\
4\text{NH}_3 + 5\text{O}_2 &\rightarrow 4\text{NO} + 6\text{H}_2\text{O}, \\
4\text{NH}_3 + 3\text{O}_2 &\rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}.
\end{align*}
\]

As can be seen from reaction (9), hydrogen stands out from the decomposition of ammonia, can interact with the residual oxygen in the chamber and nickel oxide:

\[
\begin{align*}
\text{O}_2 + 2\text{H}_2 &\rightarrow 2\text{H}_2\text{O}; \\
\text{NiO} + \text{H}_2 &\rightarrow \text{Ni} + \text{H}_2\text{O}.
\end{align*}
\]

Assuming that the nitrogen as an inert gas and it does not react with structure materials and evacuated by vacuum system, it is necessary to consider the interaction between the silicon and probable chromium oxides:

\[
\begin{align*}
11\text{Si} + 10\text{CrO} &\rightarrow 5\text{SiO}_2 + 2\text{Cr}_3\text{Si}_3; \\
3\text{Si} + \text{Cr}_2\text{O}_3 &\rightarrow \text{Si}_2\text{O}_3 + \text{CrSi}_2; \\
11\text{Si} + 2\text{Cr}_2\text{O}_3 &\rightarrow 3\text{SiO}_2 + 4\text{CrSi}_2.
\end{align*}
\]

For reduction of the catalyst in the CVD module uses "activation" stage, which consists in applying and holding the sample in a higher concentration ammonia (210 cm\(^3\)/min) (as compared to the heating step) after reaching the set temperature. Consider the interaction of the components of the sample structure after heating with the products of decomposition of ammonia at the stage of activation:

\[
\begin{align*}
\text{NiO} + \text{H}_2 &\rightarrow \text{Ni} + \text{H}_2\text{O}; \\
\text{CrO} + \text{H}_2 &\rightarrow \text{Cr} + \text{H}_2\text{O}; \\
\text{Cr}_2\text{O}_3 + 2\text{H}_2 &\rightarrow 2\text{Cr} + 3\text{H}_2\text{O}.
\end{align*}
\]

On growth stage in CVD chamber fed ammonia (210 cm\(^3\)/min) and acetylene (70 cm\(^3\)/min).

The reactions of the interaction of the sample components with acetylene:

\[
\begin{align*}
6\text{Ni(sol)} + \text{C}_2\text{H}_2 &\rightarrow 2\text{Ni}_3\text{C(sol)} + \text{H}_2; \\
6\text{Ni(liq)} + \text{C}_2\text{H}_2 &\rightarrow 2\text{Ni}_3\text{C(liq)} + \text{H}_2; \\
9\text{CrO} + \text{C}_2\text{H}_2 &\rightarrow \text{Cr}_3\text{C}_2 + \text{H}_2 + 3\text{Cr}_2\text{O}_3; \\
3\text{Cr}_2\text{O}_3 + 4\text{C}_2\text{H}_2 &\rightarrow \text{Cr}_3\text{C}_2 + 4\text{H}_2 + 6\text{CO}; \\
6\text{Cr}_2\text{O}_3 + 13\text{C}_2\text{H}_2 &\rightarrow 4\text{Cr}_3\text{C}_2 + 13\text{H}_2 + 18\text{CO}; \\
\text{Ni}_3\text{C(sol)} &\rightarrow 3\text{Ni(sol)} + \text{C}; \\
\text{Ni}_3\text{C(liq)} &\rightarrow 3\text{Ni(liq)} + \text{C}.
\end{align*}
\]

3. Results and discussion

Results of calculation of Gibbs potential for given Ni oxidation reactions (3) - (4), and Cr (5) shown in Figure 1 (a), (b) - respectively. Analysis of dependencies \(\Delta G(T)\) (3) - (4) at a pressure of 4.5 Torr showed that the most likely Ni oxidation reaction of residual oxygen, since Ni does not react with water. Thus Ni oxidized by oxygen from the atmosphere and forms a NiO oxide, and contacting with
Cr reduced to pure Ni with the formation of chromium oxide. However, the continued flow of oxygen from the atmosphere contributes to oxidation of Ni film until chromium is not enough of oxygen to form stable chromium oxide Cr$_2$O$_3$ (Figure 1 (b)).

Thus, before beginning the process of formation of CC and growing CNTs should be noted that the underlayer film and the catalyst can be oxidized. Also, direct interaction of Ni and Cr at the used in CVD process conditions can be excluded, because up to 1800 °C Ni and Cr do not interact [11].

It is found that on the heating stage ammonia is decomposed into N$_2$ and H$_2$ under the influence (figure 2 (a)). A thermodynamic analysis of reaction (12) (13) (figure 2 (b)) showed that hydrogen produced by the decomposition of ammonia, can interact with the residual oxygen in the chamber, and with nickel oxide. Thus these reactions are competing.

According to the results of analysis of dependencies ΔG(T) (figure 3) revealed that the presence of ammonia of relatively low concentration (15 cm$^3$/min) cleans chamber from the residual
oxygen through vapor oxidation of free hydrogen produced by the decomposition of ammonia to form water vapor. At the same time, formed water vapor evacuated by vacuum system that allows clean the chamber. However, reduction of NiO in a low ammonia concentration is not possible.

From the calculations of Gibbs potential of interaction of silicon with the possible oxides of chromium, it can be concluded that the most likely formation CrSi2 and SiO2 (figure 3 (a)).

![Figure 3. Chemical reactions in structure: a) the temperature dependence of the Gibbs energy change for reactions (14)-(16) on heating stage; b) Ni and Cr reduction on activation stage](image)

The results of calculation of the Gibbs potential for nickel and chromium reduction reactions at the activation stage (figure 3 (b)) showed that the activation stage is accompanied by reduction of Ni. At the same time restore the chromium oxide with given technological modes is not possible.

Dependencies of the Gibbs potential for the reactions occurring on the growth stage presented in figure 4.

![Figure 4. The temperature dependence of the Gibbs energy change on growth stage for reactions: a) interaction of CrxOy with C2H2; b) interaction of Ni (solid and liquid) with C2H2 and decomposition of Ni3C (solid and liquid).](image)

Figure 4 (a) shows that the underlayer during the growth stage can be transformed to a mixture of Cr2O3 + Cr3C2, and figure 4 (b) shows that acetylene decomposes on Ni catalytic centers to form nickel carbide, regardless of what phase it is (solid or liquid). Obtained by decomposition of acetylene on the catalytic centers, nickel carbide is an unstable compound and decomposes with the release of carbon (reactions (26), (27)). As a result, CNTs are formed by self-organization effect.
Conclusion

As a result of chemical analysis of the thermodynamic processes taking place in the structure of Ni/Cr/Si found that during mounting the sample in the CVD chamber and subsequent heating material of Ni/Cr/Si structure is oxidized. Thus Cr underlayer oxidation occurs due to the exchange reaction of Cr with NiO, with the formation of chromium oxide. On heating stage occurs chamber cleaning process of unwanted residual water vapor and oxygen, as well as the formation of chromium silicide layer. The presence of an oxidized catalyst (NiO) requires an additional stage of recovery. On activation stage take place reactions of Ni recovery resulting in full catalyst reduction that can be used for the subsequent growth of nanotubes. It is shown that reduction of the underlayer of chromium oxide with given parameters of the process is not possible. Thus, under the Ni catalytic layer formed underlayer with complex composition Cr/CrOx/CrSi2, which act as a diffusion barrier to the interaction of the Ni and the Si substrate. It is found that on growth stage occurs decomposition of acetylene on Ni catalyst centers, with release of free carbon. In this case, the underlayer may form a solid solution of a mixture Cr2O3 + Cr3C2.

The obtained data allow to optimize the process of growing CNTs by the CVD method to produce less defective nanotubes, as well as to optimize the methodology for the selection of the underlayer material to form a conductive contact to the CNT, which is necessary for the creation of micro- and nanoelectronic devices.

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