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SYNTHESIS OF CARBON NANOTUBES WITH NI-TI CATALYST

Abstract. Carbon nanotubes have been of interest to the scientists for about 30 years due to their unique properties. Their use as a material for creating flexible conductive coatings, supercapacitors, batteries and solar cells is promising because of their excellent mechanical and electrical properties, as well as high electrochemical stability. In this paper, we consider one of the methods for the synthesis of carbon nanotubes on a Ni-Ti bimetallic catalyst on a silicon substrate. The effect of the thickness of the catalytic layer and the synthesis temperature on the quality of the obtained samples was studied. The synthesis was carried out by the CVD method as the most convenient technique with the possibility of a large yield of the final product. The obtained samples were studied by scanning electron microscopy and Raman spectroscopy. It was found that with an increase in the synthesis temperature and a decrease in the thickness of the catalytic layer, the crystallinity of the structure improves the number of defects in the structure decreases and structural ordering increases. The use of a catalyst and an adhesive metal layer, which was a barrier between the catalyst and the substrate, shows good results in improving the quality of the synthesis of nanotubes.

Keywords: carbon nanotubes, synthesis, chemical vapor deposition (CVD), catalyst, magnetron sputtering.

Introduction. A carbon nanotube is a hollow cylindrical structure with a diameter of one to several tens of nanometers, a length of one to several hundred micrometers or more, formed by carbon atoms and is a graphene plane rolled into a cylinder. For the first time, CNTs were systematically described by Sumio Iijima (NEC Corporation), who discovered them in 1991 as a by-product of the synthesis of fullerene C₆₀ [1], and, almost simultaneously with it, the L.A. group Chernozatonsky [2]. Mention of the existence of unusual forms of carbon similar in morphology was encountered earlier [3, 4], however, these works did not receive further development.

Carbon nanotubes (CNTs) have many physical and chemical properties many of which are unique. CNTs have very high thermal conductivity [5,6], strength [7], and the tensile modulus is many times higher than that of steel. A wide range of electrical conductivity [8, 9] from semiconductor to metal makes them promising for creating conductors and pn junctions in nanoelectronics, for creating conductive high-strength composite materials and functional additives to polymers. The use of carbon nanotubes in various fields of science and technology is a promising task [10]. In addition, carbon materials, such as amorphous carbon or activated carbon, are widely used, and their replacement with CNTs in some cases gives a unique effect, limited only by the higher cost of CNTs compared to other carbon materials. Therefore, the development of effective methods for the synthesis of CNTs is a very urgent task.

CVD is a method with a high level of process control that allows you to control the growth location and geometric parameters of carbon tubes on any type of substrate [11]. To obtain an array of CNTs on the substrate surface, a seed layer is needed. A thin metal film acts as a seed layer, which is a catalyst for the growth of CNTs; mainly nickel, iron, and cobalt act as such metals. A catalyst film can be formed using

the methods of chemical deposition from a solution containing a catalyst, thermal evaporation, ion beam sputtering, or magnetron sputtering. The main issue of this work was to study the effect of a buffer layer, as well as the temperature dependence and thickness of the catalytic layer on the growth of CNTs.

Experiment. In this work, a bimetallic catalyst was used to synthesize CNTs. Its preparation included 2 stages: the deposition of a catalytic layer and the formation of nanoclusters. At the first stage, a thin layer of titanium with a thickness of 80 nm is deposited on the pre-cleaned substrate using the magnetron sputtering method. After that, 0.5 to 10 nm thick nickel layers were deposited using the second magnetron, which is in the same chamber. The thickness of the forming layer is adjusted according to the indications of quartz microbalances previously calibrated for the sputtered materials. The second stage is the formation of nanoclusters, which occurs during the replacement of the substrate from the cold zone of CVD the reactor to a hot one, pre-heated to the synthesis temperature. Within 5 minutes after the placement of the substrate into the hot zone, the catalyst film transforms into nanoclusters. The process takes place in a stream of hydrogen, which reduces the catalyst because thin metal films oxidize very quickly in the air. This is necessary for high catalytic activity. A longer heating duration leads to an increase in the particle size of the catalyst, which in turn affect the tubes' diameter. The synthesis of CNTs by the CVD method of was carried out in a tubular sealed quartz reactor at atmospheric pressure in a stream of hydrogen equal to 4 normal liters per hour (figure 1). The carbon source in the synthesis process was ethanol vapor. In the preparation stage for the synthesis, the chamber while heating was preliminary blown out with nitrogen for 10 minutes to remove oxygen, and only after that the hydrogen was let into the chamber. In addition, at the stage of the heating, the hydrogen passed through the bubbler previously blowing all the air out of volume unfilled with ethanol. The bubbler and the reaction zone of the chamber were cut out with valves, which were opened only at the time of synthesis. The flow of hydrogen passing through a bubbler carries the ethanol vapour into the reaction zone of the chamber, where under the high temperature the ethanol decomposes into carbon and hydroxyl group. The latter in turn combines with hydrogen, forming water vapor or interacting with an amorphous carbon formed in the process of the synthesis, oxidizing it this way and removing from the substrate increasing the catalyst activity time. We experimentally found out an optimal temperature for our chamber configuration. It ranges from 880°C to 950°C. Upon reaching the synthesis temperature, a stream of hydrogen is directed through a bubbler with ethanol at room temperature. Upon completion of the synthesis, the hydrogen flow is stopped and the bubbler is cut out with valve. Samples were taken into the cold zone. Subsequent cooling of the reactor took place in a stream of nitrogen. After taking the samples out the reactor, one can see that the substrates are covered with a soot.

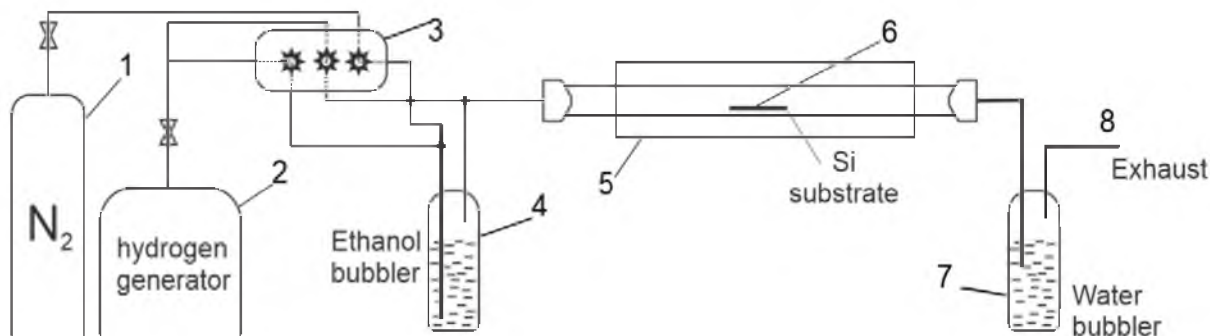


Figure 1 - The structure of the CVD installation for the synthesis of carbon nanomaterials.
1 - nitrogen gas, 2 - hydrogen generator, 3 - gas flow meters, 4 - bubbler with ethanol, 5 - tubular flow reactor, 6 - substrate, 7 - bubbler with water for gas purification, 8 - discharge to the atmosphere

Figure 2 shows silicon substrates coated with a nickel-titanium catalyst before and after the synthesis of CNTs by CVD. It is seen that after the synthesis the substrate surface with catalyst layer is covered with soot, which indicates the possible deposition of carbon nanostructures, including CNTs.

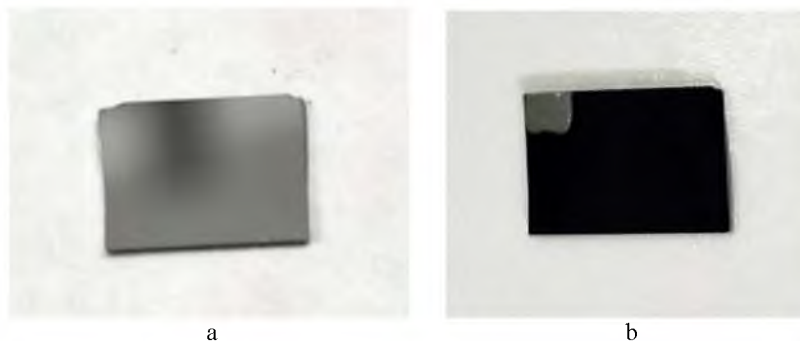


Figure 2 - Silicon substrates with a nickel-titanium catalyst
(a) - before and (b) after synthesis of CNTs by CVD

Results and discussions. It is known from the literature [12] that the average size of catalyst nanoclusters formed after annealing depends on the thickness of the initial film, as well as the duration of heating of the substrate. During our experiments, it was found out that the synthesis temperature plays a key role in this process, because at different thicknesses of the deposited catalyst layer and at the same annealing temperature, the diameters of the tubes are the same. However, with an increase in the synthesis temperature, the diameter of CNTs decreases significantly. Using SEM analysis, talking about the diameter of the tubes is only conditional. However, this analysis shows a significant change in size with increasing temperature (figure 4-5).

To improve the quality of the synthesized CNTs, the so-called titanium buffer layer was used in this work. As the experimental results show, in the absence of a buffer layer during high-temperature heating, the silicon substrate material interacts with the catalyst, leading to the formation of nickel silicide islands [13] (figure 3a). As can be seen from Figure 3b, CNT growth occurs only on these areas. On the rest of the substrate, where no islands are formed, the catalyst loses its activity, possibly due to the diffusion process into the surface of the substrate (figure 3c).

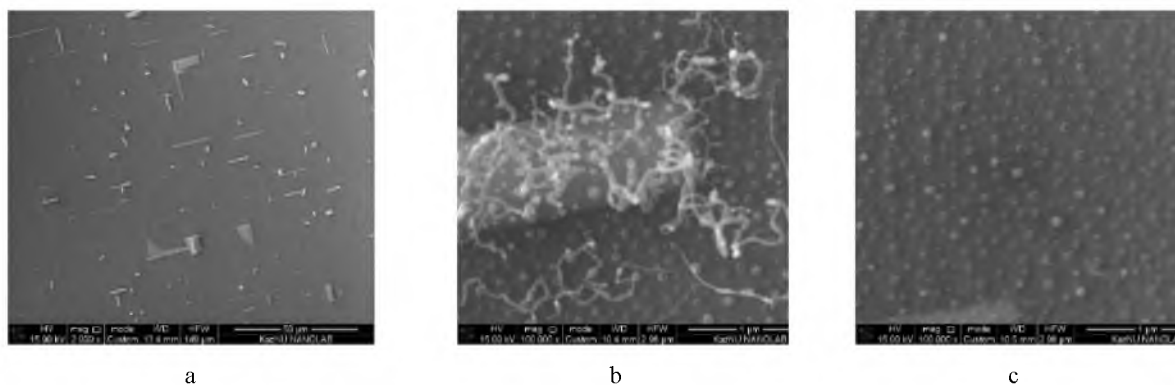
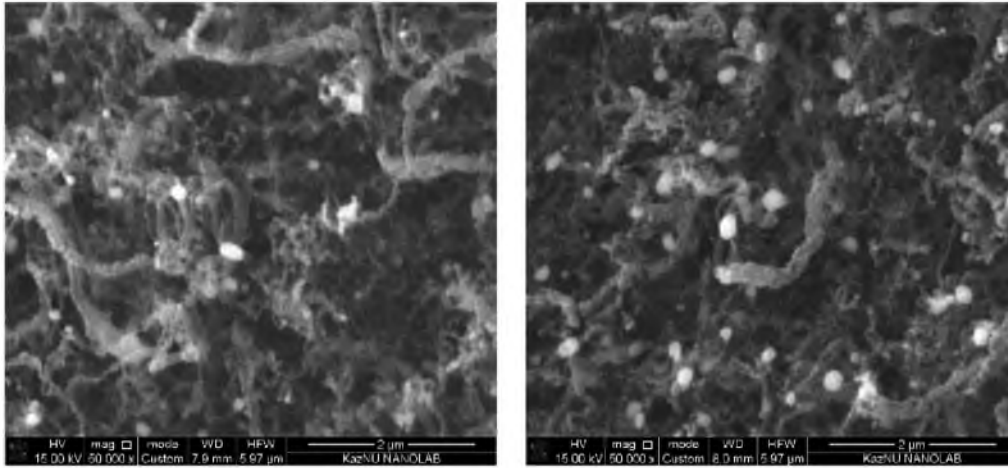


Figure 3 - The formed islands of nickel silicide (a) and selective growth of CNTs on it (b,c)

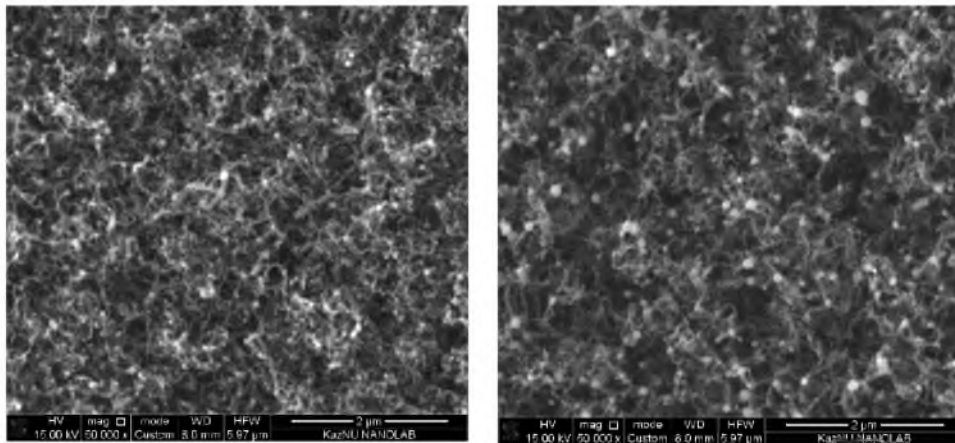
Thus, to prevent the diffusion of nickel into silicon and the formation of nickel silicide, a thin film of a titanium buffer layer was deposited on the silicon surface. Under the high temperature, a titanium-nickel alloy is formed, which subsequently exhibits high catalytic activity. An analysis of the results showed that an increase in the synthesis temperature affects the quality of the obtained samples. The properties of these samples were studied by scanning electron microscopy (figure 4-5) and Raman spectroscopy (figure 6). Raman signal of the synthesized products corresponds to a typical spectrum of multi-walled carbon nanotubes (MWCNTs) [14]. Analysis of the Raman data shows that with increase in the synthesis temperature, the quality of the obtained samples improves; this is evidenced by an increase in the G peak's intensity and a decrease of the D peak intensity (characterizing the defective structure).



a – Ni (5 nm), Ti (80 nm)

b – Ni (10 nm), Ti (80 nm)

Figure 4 - CNT samples synthesized at a temperature of 880°C and synthesis time t - 1 min



a – Ni (5 nm), Ti (10 nm)

b – Ni (10 nm), Ti (80 nm)

Figure 5 - Samples of MWCNTs synthesized at a temperature of 950°C and synthesis time t - 1 min

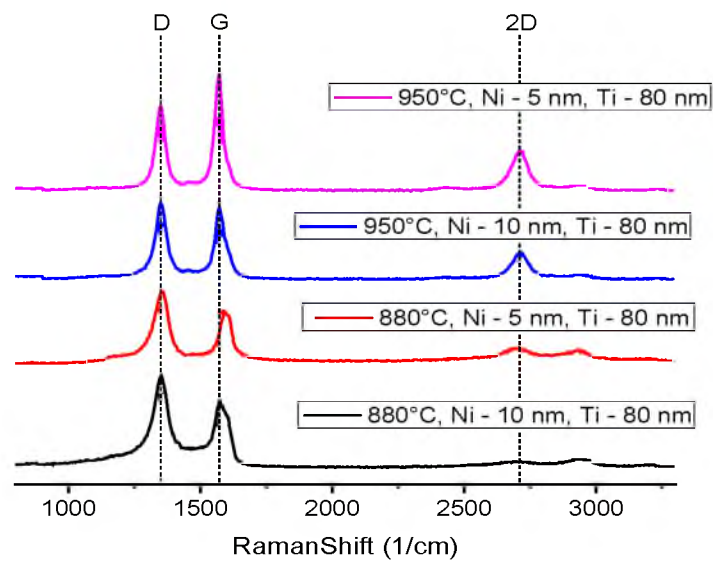
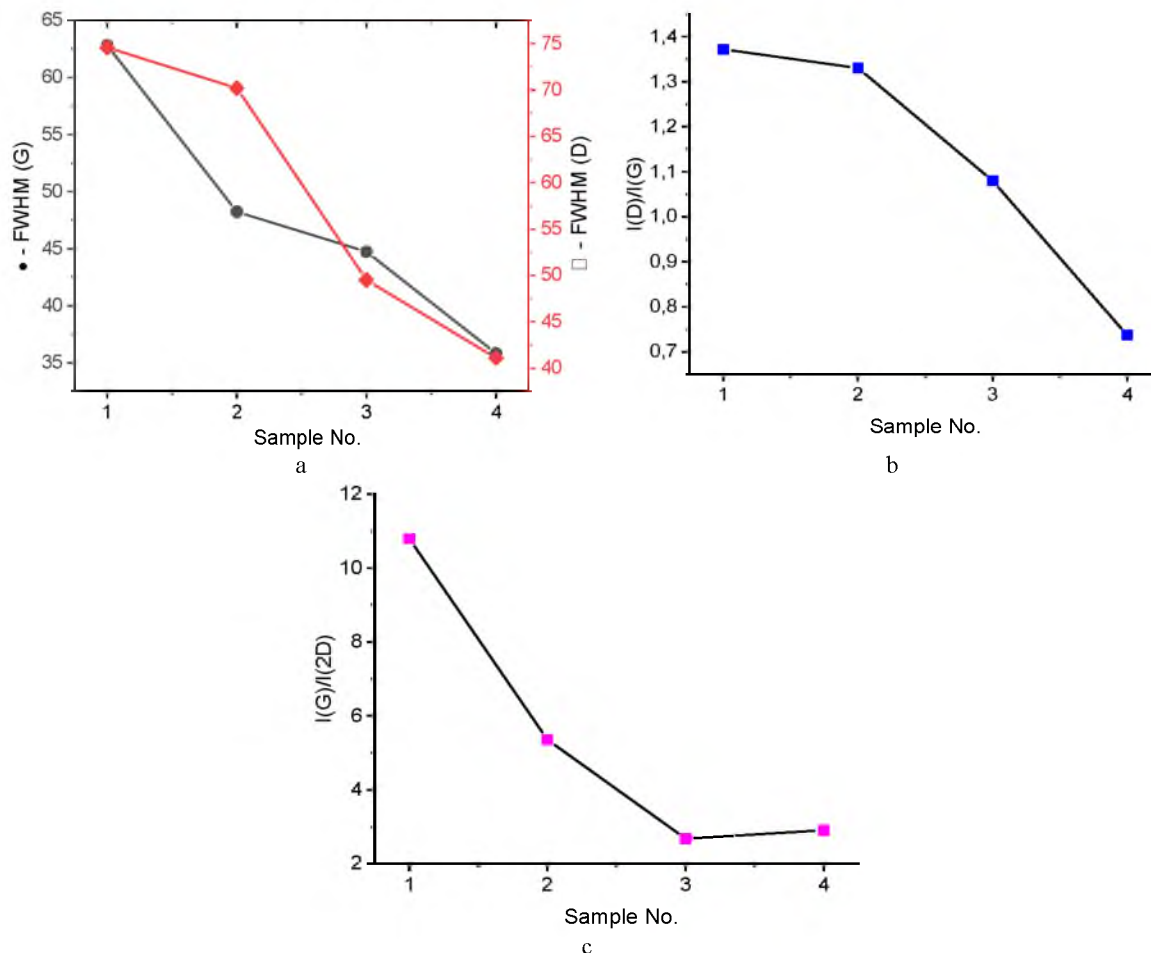


Figure 6 - Raman spectra of obtained MWCNTs



where No. 1 and No. 3 are samples of Ni (10 nm), Ti (80 nm), T = 880 and 950 °C, respectively, No. 2 and No. 4 are samples of Ni (5 nm), Ti (80 nm), T = 880 and 950 °C, respectively

Figure 7 - Data analysis of the Raman spectra of CNTs

A more detailed analysis of the Raman spectra of CNTs is presented in figure 7. It can be seen that with increasing temperature and decreasing thickness of the catalytic layer, such trends are observed: narrowing of the half-width of the peaks (figure 7a), which indicates an increase in the crystallinity of the structure; a decrease in the intensity of peak D, which is represented by the ratio $I(D)/I(G)$, indicating a decrease in the number of defects in the structure (figure 7b); a decrease in the ratio of G to 2D peaks' intensity, which indicates an increase in structural ordering in the mutual arrangement of atoms (figure 7c) [15-16]. Thus, it was shown in the work that the use of a titanium buffer layer allows to reach effective synthesis conditions, while the diameters and quality of synthesized CNTs depend not only on the thickness of the catalytic film but also on the synthesis temperature.

Conclusion. Due to its variability, the CVD method makes it possible to precisely control the growth of CNTs. By changing the synthesis parameters, one can control the yield and structural parameters of nanotubes. In this work, the influence of the synthesis temperature and the thickness of the catalytic layer on the growth of CNTs, as well as the role of the buffer layer, were demonstrated. An increase of synthesis temperature and a decrease in the thickness of the catalyst improves the crystallinity of nanotubes. The use of a catalyst and an adhesive metal layer, which was a barrier between the catalyst and the substrate, gave positive results in improving the effectiveness of the synthesis of nanotubes. It was previously assumed that the catalyst particles during preliminary annealing can dissolve in titanium and lose their catalytic activity; however, the formed Ti-Ni nanoclusters promoted the catalytic growth of CNTs.

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КӨМІРТЕКТІ НАНОТҮТІКШЕЛЕРДІ Ni-Ti КАТАЛИЗАТОРЫМЕН СИНТЕЗДЕУ

Аннотация. Отыз жыл бойы көміртекті нанотүтікшелер ерекше қасиетінің арқасында ғалымдарды қызықтырып келеді. Оларды икемді өткізгіш жабын, суперконденсатор, батареялар мен күн батареяларын жасау үшін материал ретінде пайдалану тамаша механикалық және электрлік қасиеттері арқылы әрі жоғары электрохимиялық тұрақтылығымен ерекшеленеді. Мақалада кремний субстратындағы Ni-Ti биметалды катализаторында көміртекті нанотүтікшелерді синтездеу әдістерінің бірін қарастырамыз. Каталитикалық қабаттың қалыңдығы мен синтез температурасының алынған үлгілердің сапасына әсері де зерттелді. CVD синтезді соңғы өнімнің үлкен шығымдылығы арқылы ықтимал ең қолайлы өндіріс әдісі ретінде жүргізді. Алынған үлгілер сканерлеуші электронды және Раман спектроскопиясы арқылы зерттелді. Синтез температурасының өсуі және каталитикалық қабаттың қалыңдығының азаюы негізінде құрылым кристалдылығының жақсаруы, ақау санының азаюы және құрылымдық реттіліктің жоғарылауы байқалды. Катализатор мен төсеніш арасындағы кедергі саналатын, катализатор мен металдың адгезиялық қабатын пайдалану, көміртекті нанотүтікшелер синтезінің сапасын жақсартуда оң нәтиже берді.

Көміртекті нанотүтікше – қуыс цилиндрлік құрылым, диаметрі бірнеше нанометрден басталып ондаған нанометрлерге дейін жететін, ұзындығы бір микрометрден жүздеген микрометрге дейін немесе одан да көп болатын, көміртек атомдарынан түзілген және цилиндрге оралған графен парақшасы. Алғаш рет КНТ жүйелі түрде Сумио Ииджима (Sumio Iijima NEC Corporation) сипаттады, ол оларды 1991 жылы C60 фуллерендер синтезінің жанама өнімі ретінде ашты және онымен бір мезгілде Л.А.Чернозатонскийдің тобы да сипаттаған. Морфологиясы көміртектің ұқсас ерекше формаларының бар екендігі туралы бұрын да кездестірілген, алайда бұл жұмыстар одан әрі дами алмады.

Көміртекті нанотүтікшелер (КНТ) көптеген физикалық және химиялық қасиеттерге ие, олардың көпшілігі ерекше болып келеді. КНТ өте жоғары жылу өткізгіштікке және беріктікке ие, ал созылу модулі болатқа қарағанда бірнеше есе жоғары. Жартылай өткізгіштен металға дейінгі электр өткізгіштіктің кең спектрі оларды наноэлектроникада өткізгіштер мен р-п жартылай өткізгіш құруға, өткізгіштігі жоғары берік композит материалдар мен полимерлерге функционалды қоспалар жасауға КНТ перспективалы етеді. Көміртекті нанотүтікшелерді ғылым мен техниканың әртүрлі саласында қолдану перспективалы тапсырма болып есептеледі. Сонымен қатар, көміртегі материалдары, мысалы, аморфты көміртек немесе активтендірілген көміртек, кеңінен қолданылады және оларды КНТ-мен алмастыру кей жағдайда ерекше эффект береді, алайда басқа көміртекті материалдармен салыстырғанда КНТ қымбат болғандықтан шектеледі. Сондықтан КНТ синтезінің тиімді әдістерін жасау өте өзекті болып саналады.

CVD – кез-келген субстратқа көміртек түтікшелерінің өсу орны мен геометриялық параметрлерін бақылауға мүмкіндік беретін жоғары технологиялық бақылау әдісі. Субстрат бетіне КНТ массивін алу үшін тұқым қабаты қажет. Жұқа металл қабыршағы тұқым қабаты ретінде әрекет етеді әрі КНТ өсуінің катализаторы болып саналады, негізінен металл ретінде никель, темір және кобальт қолданылады. Катализатор қабыршағын алу үшін катализаторы бар ерітіндіден химиялық тұндыру, термиялық булану, иондық сәулелің шашылуы немесе магнетронның шашырау әдістерін қолдану арқылы қол жеткізуге болады. Бұл жұмыстағы басты мәселе КНТ өсуіне буфер қабатының болуы, сонымен қатар катализатор қабаттың қалыңдығы және синтез температурасына тәуелділік әсерін зерттеу.

Түйін сөздер: көміртекті нанотүтікшелер (КНТ), синтез, химиялық будың тұнбасы (CVD), катализатор, магнетронды шашырату.

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СИНТЕЗ УГЛЕРОДНЫХ НАНОТРУБОК НА КАТАЛИЗАТОРЕ Ni-Ti

Аннотация. Углеродные нанотрубки в течение последних 30 лет, благодаря своим уникальным свойствам, представляют интерес для ученых. Их использование в качестве материала для создания гибких проводящих покрытий, суперконденсаторов, батарей и солнечных элементов является перспективным ввиду того, что они обладают превосходными механическими и электрическими свойствами, а также высокой электрохимической стабильностью. В этой статье рассматривается один из методов синтеза углеродных нанотрубок на Ni-Ti биметаллическом катализаторе на поверхности кремниевой подложки. Также изучено влияние толщины каталитического слоя и температуры синтеза на качество полученных образцов. Синтез проводился методом CVD как один из наиболее распространённых методов получения наноматериалов с большим количественным выходом конечного продукта. Полученные образцы были изучены методами сканирующей электронной микроскопии и спектроскопии комбинационного рассеяния. Обнаружено, что с ростом температуры синтеза и уменьшением толщины каталитического слоя наблюдается улучшение кристалличности структуры, уменьшение количества дефектов и рост структурной упорядоченности. Использование катализатора и адгезионного слоя металла, который являлся барьером между катализатором и подложкой, дало положительные результаты в улучшении качества синтеза углеродных нанотрубок.

Углеродная нанотрубка – это полая цилиндрическая структура диаметром от нескольких до нескольких десятков нанометров, длиной от одной до нескольких сотен микрометров и более, образованная атомами углерода и представляющая собой плоскость графена, свёрнутую в цилиндр. Впервые УНТ систематически описаны Сумио Ииджимой (Sumio Iijima, корпорация NEC), обнаружившего их в 1991 г. как побочный продукт синтеза фуллерена C₆₀, и практически одновременно с ним – группой Л.А. Чернотановского. Упоминания о существовании схожих по морфологии необычных форм углерода встречались и раньше, однако дальнейшего развития эти работы тогда не получили.

Углеродные нанотрубки (УНТ) обладают множеством физических и химических свойств, многие из которых уникальны. УНТ имеют очень высокую теплопроводность и прочность, а модуль упругости при растяжении во много раз выше, чем у стали. Широкий диапазон электропроводности от полупроводника до металла делает их перспективными для создания проводников и рп-переходов в нанoeлектронике, для создания проводящих высокопрочных композитных материалов и функциональных добавок к полимерам. Применение углеродных нанотрубок в различных областях науки и техники является перспективной задачей. Кроме того, углеродные материалы, такие как аморфный углерод или активированный уголь, широко применяются, и их замена на УНТ в некоторых случаях даёт уникальный эффект, ограниченный только более высокой стоимостью УНТ по сравнению с другими углеродными материалами. Поэтому разработка эффективных методов синтеза УНТ очень актуальна.

CVD является методом с высоким уровнем контроля процесса, который позволяет контролировать местоположение роста и геометрические параметры углеродных трубок на любом типе подложки. Чтобы получить массив УНТ на поверхности подложки, нужен затравочный слой. В качестве затравочного слоя выступает тонкая плёнка металла, которая является катализатором для роста УНТ, в роли таких металлов выступают в основном никель, железо и кобальт. Нанесение плёнки катализатора возможно с использованием методов химического осаждения из раствора, содержащего катализатор, термического испарения, ионно-лучевого распыления или магнетронного распыления. В качестве основного вопроса в данной работе было исследование влияния наличия буферного слоя, а также температурная зависимость и толщина каталитического слоя на рост УНТ.

Ключевые слова: углеродные нанотрубки (УНТ), синтез, химическое осаждение из паровой фазы (CVD), катализатор, магнетронное распыление.

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