

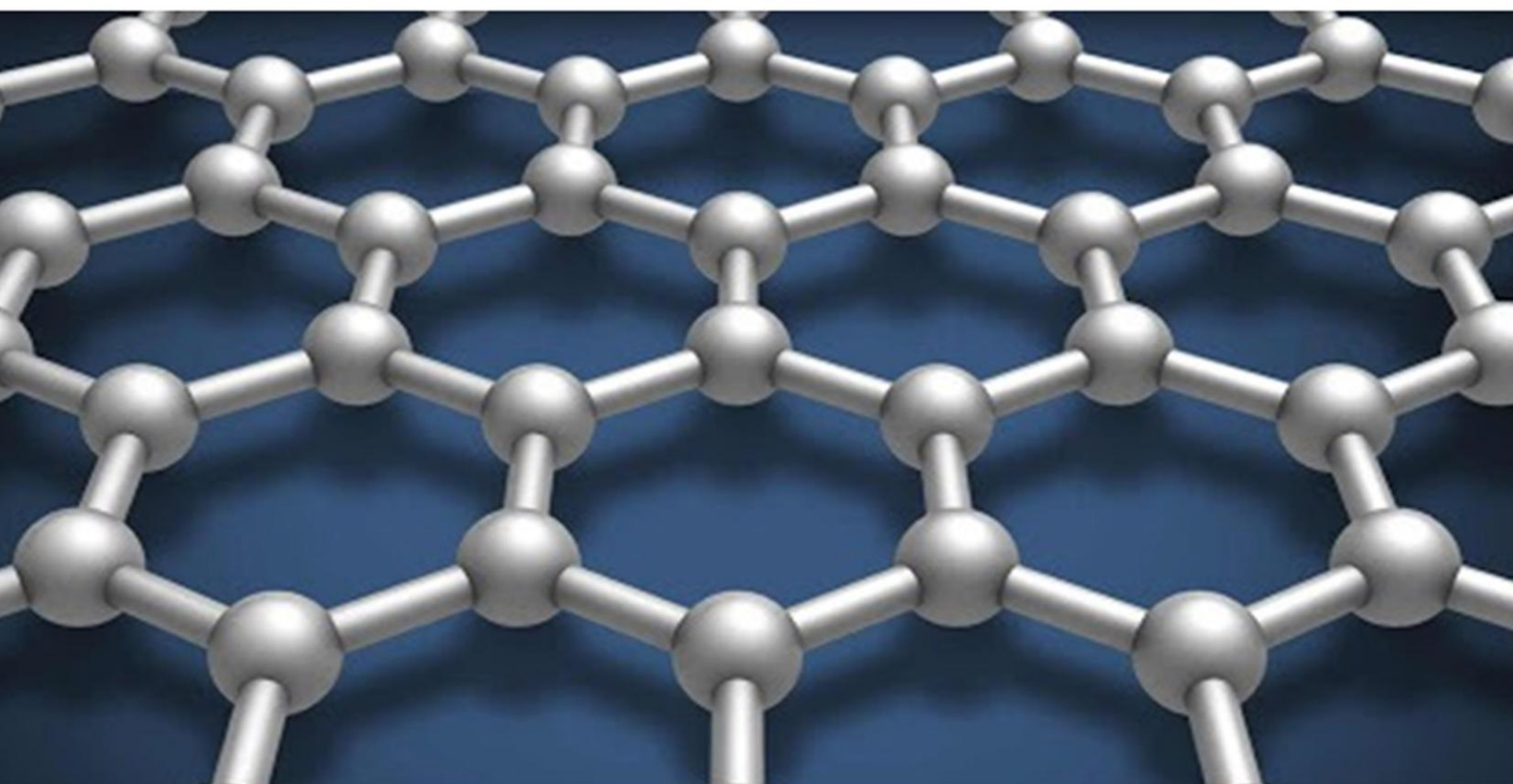
ISSN 2091-5527

№ 3/2026

O'zbekiston

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Ilmiy-texnikaviy va amaliy jurnali



Узбекский научно-технический и производственный журнал
Композиционные материалы

UDC: 546.26-162:543.424.2

EFFECT OF METHANE FLOW RATE ON THE RAMAN CHARACTERISTICS AND SPATIAL UNIFORMITY OF CVD GRAPHENE GROWN ON HIGH-PURITY COPPER AT 1020 °C**Tursunkulov O.M.*, Gulyamov B.B., Sobitov M.A., Abduqahhorov F.I.,
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Abstract. Graphene was grown by chemical vapor deposition on high-purity polycrystalline Cu at 1020 °C while CH₄ flow was varied from 20 to 1 sccm at a constant H₂ flow of 20 sccm. Pressure and process times were fixed. XRD showed that the CVD cycle enhanced the Cu(200)-dominated texture without a significant lattice change or detectable bulk Cu-oxide phase. Nine Raman spectra, three per flow condition, were fitted independently. H₂:CH₄ = 20:1 gave the most reproducible response: I_D/I_G = 0.072 ± 0.015, I_{2D}/I_G = 1.809 ± 0.076 and FWHM(2D) = 44.03 ± 1.41 cm⁻¹. Higher methane flows produced greater point-to-point dispersion. Reduced methane delivery therefore provided the best balance of weak defect scattering, narrow 2D bands and Raman-scale uniformity, consistent with monolayer-like or thin few-layer graphene.

Keywords: graphene; chemical vapor deposition; methane flow rate; Raman spectroscopy; spatial uniformity; copper; PMMA-free transfer.

1. Introduction. Chemical vapor deposition (CVD) on Cu is widely used for large-area graphene because the low carbon solubility of Cu favors surface-mediated growth [1]. At fixed temperature, methane supply and hydrogen-assisted surface reactions influence nucleation, domain coalescence, layer overlap and defect formation [2–4]. Transfer can additionally introduce cracks, folds, residues and non-uniform doping [5]. Raman D, G and 2D bands provide complementary measures of disorder, sp² bonding and layer-sensitive electronic structure [6,7]. Because a single spectrum may conceal spatial variation, this work compares three positions for each of three CH₄ flows at 1020 °C and uses correlated G/2D shifts only as qualitative strain–doping indicators [8].

2. Experimental. High-purity Cu foil (Alfa Aesar Puratronic, 99.9999%, 0.05 mm) was cut into 40 × 50 mm pieces, solvent-cleaned and placed in a horizontal quartz-tube reactor. All runs were performed at 1020 °C and approximately 0.5 Torr. Cu was annealed for 60 min under 20 sccm H₂; graphene was then grown for 30 min with CH₄ flows of 20, 10 or 1 sccm while H₂ remained at 20 sccm. The resulting H₂:CH₄ conditions were 20:20, 20:10 and 20:1. Cooling used 100 sccm Ar. Thus, only methane flow was deliberately varied (Table 1).

Transfer. Graphene/Cu was floated on Nickel Etchant Type I, rinsed in three distilled-water baths, collected on SiO₂ and dried without PMMA or post-transfer annealing.

Table 1.**Principal CVD parameters for graphene growth on high-purity Cu at 1020 °C.**

Parameter	H ₂ :CH ₄ = 20:20	H ₂ :CH ₄ = 20:10	H ₂ :CH ₄ = 20:1
Growth temperature, °C	1020	1020	1020
H ₂ flow, sccm	20	20	20
CH ₄ flow, sccm	20	10	1
Working pressure, Torr	~0.5	~0.5	~0.5
H ₂ annealing time, min	60	60	60
CH ₄ growth time, min	30	30	30
Ar cooling flow, sccm	100	100	100

XRD. Cu before and after CVD was measured in coupled θ – 2θ geometry with Cu radiation (30 kV, 10 mA), a 0.0400° step and 16.5 s per step. The common 27.50–89.98° interval was analyzed in HighScore+. Because the graphitic (002) region was outside the scan and the graphene volume was negligible relative to Cu, XRD was used to assess substrate texture rather than graphene thickness.

Raman spectroscopy. Spectra were recorded at room temperature with 514.5 nm excitation, a ×50 objective and 10 s acquisition at three positions (P1–P3) per condition. Unscaled spectra were fitted by a local quadratic background and single Lorentzian

profiles over the D (1240–1475 cm⁻¹), G (1480–1685 cm⁻¹) and 2D (2500–2875 cm⁻¹) ranges. Peak heights gave I_D/I_G and I_{2D}/I_G; uncertainties are sample standard deviations. Pairwise checks confirmed nine distinct intensity vectors, so n = 3 for each condition. Figure 2 alone uses baseline-corrected, G-normalized and vertically offset traces; quantitative fits used unscaled data.

3. Results and Discussion. 3.1. XRD of the Cu substrate. Before CVD, reflections at 43.4676°, 50.6019° and 74.2913° were assigned to fcc-Cu (111), (200) and (220), with relative intensities of 20.77, 100 and 3.44%. After the 1020 °C cycle,

Cu(200) at 50.6128° dominated, and its fitted height and area rose by approximately 11.74-fold. Although absolute θ - 2θ intensities depend on specimen geometry, this redistribution demonstrates stronger Cu(200)-dominated out-of-plane texture. The small shift $\Delta 2\theta = +0.0109^\circ$ corresponds to an apparent lattice change of only -0.020% and is not significant without zero-shift calibration. Weak residual features did not form a consistent CuO or Cu₂O set; therefore no distinct bulk crystalline oxide was detected, although an ultrathin or amorphous surface oxide cannot be excluded.

3.2. Multi-point Raman spectra. All nine spectra contain the D (~ 1350 cm⁻¹), G (~ 1580 cm⁻¹) and 2D (~ 2690 – 2700 cm⁻¹) bands of graphitic sp² carbon [6,7]. The 20:1 traces show the most reproducible G and 2D shapes and consistently weak D scattering (Figure 2). Representative 20:1-P2 gives $I_D/I_G = 0.071$, $I_{2D}/I_G = 1.839$ and $\text{FWHM}(2D) = 42.75$ cm⁻¹. Across 20:1, the

corresponding ranges are 0.058–0.088, 1.722–1.865 and 42.75–45.53 cm⁻¹. These narrow single-component 2D bands support a monolayer-like or thin few-layer assignment, but do not establish complete monolayer coverage [7,8].

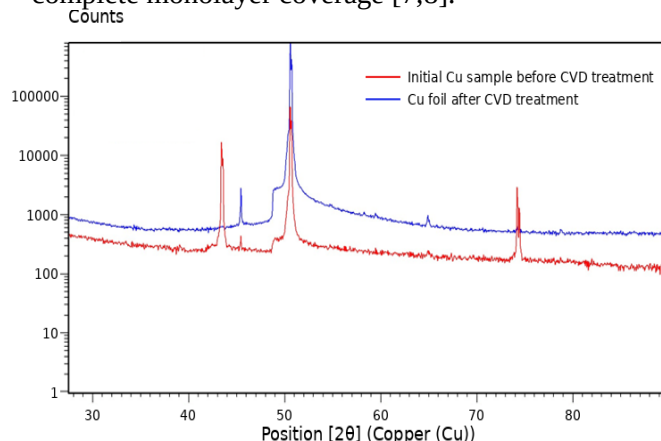


Fig. 1. XRD patterns of the initial Cu substrate (red) and the substrate after the 1020 °C CVD cycle (blue); logarithmic intensity scale.

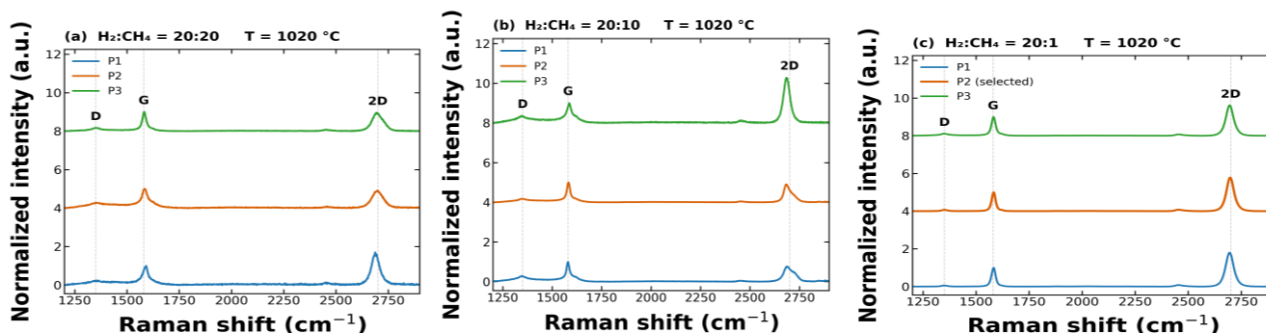


Fig. 2. G-normalized and vertically offset Raman spectra at 1020 °C for H₂:CH₄ = (a) 20:20, (b) 20:10 and (c) 20:1; each panel contains three independent positions

3.3. Raman statistics. Table 2 confirms that 20:1 is the most uniform condition: $I_D/I_G = 0.072 \pm 0.015$, $I_{2D}/I_G = 1.809 \pm 0.076$ and $\text{FWHM}(2D) = 44.03 \pm 1.41$ cm⁻¹. Its G and 2D positions are likewise compact (1582.60 ± 0.21 and 2696.19 ± 1.46 cm⁻¹). The 20:10 heterogeneity is illustrated by P3, which combines $I_{2D}/I_G = 3.163$ and $\text{FWHM}(2D) = 38.91$ cm⁻¹ with a comparatively high $I_D/I_G = 0.244$, whereas P1–P2 have $I_{2D}/I_G = 0.952$ – 1.007

and $\text{FWHM}(2D) = 53.02$ – 69.67 cm⁻¹. At 20:20, P1 has $I_{2D}/I_G = 2.091$ and $\text{FWHM}(2D) = 47.13$ cm⁻¹, but P2–P3 show ratios of 1.122–1.228 and widths of 66.91–68.82 cm⁻¹. Accordingly, the coefficient of variation of I_{2D}/I_G is 4.2% for 20:1, versus 73.8% for 20:10 and 35.9% for 20:20. Film quality is therefore judged from weak D scattering, narrow 2D width and low spatial dispersion together, rather than from the largest isolated I_{2D}/I_G value.

Table 2.

Raman parameters at 1020 °C (mean $\pm$ sample standard deviation, $n = 3$).

H ₂ :CH ₄ regime	ω_D (cm ⁻¹)	ω_G (cm ⁻¹)	ω_{2D} (cm ⁻¹)	I_D/I_G	I_{2D}/I_G	$\text{FWHM}(G)$ (cm ⁻¹)	$\text{FWHM}(2D)$ (cm ⁻¹)
20:20 ($n = 3$)	1351.05 ± 1.13	1585.63 ± 3.00	2695.30 ± 5.34	0.124 ± 0.017	1.480 ± 0.531	27.31 ± 4.76	60.95 ± 12.01
20:10 ($n = 3$)	1346.63 ± 1.50	1583.05 ± 3.19	2691.25 ± 5.36	0.189 ± 0.071	1.708 ± 1.261	21.45 ± 5.07	53.87 ± 15.39
20:1 ($n = 3$)	1350.60 ± 0.55	1582.60 ± 0.21	2696.19 ± 1.46	0.072 ± 0.015	1.809 ± 0.076	22.10 ± 0.76	44.03 ± 1.41

3.4. Raman correlations. In the ω_G – ω_{2D} plane, 20:1 forms the tightest cluster (Figure 3a). The overall fit (slope -1.059 ; $r = -0.617$, $R^2 = 0.380$, $p = 0.077$) is neither significant nor aligned with a single pure-strain or pure-doping trajectory; the reference directions [8] are therefore qualitative only. Absolute strain and carrier density were not calculated because a calibrated neutral reference

and dense spatial mapping were unavailable, while local stacking and transfer stress can shift both bands. The relation between I_D/I_G and $\text{FWHM}(2D)$ is also weak ($r = 0.259$, $R^2 = 0.067$, $p = 0.501$; Figure 3b). The defensible observation is group-level: 20:1 clusters at low defect response and narrow 2D width, whereas higher methane flows give broader spatial distributions.

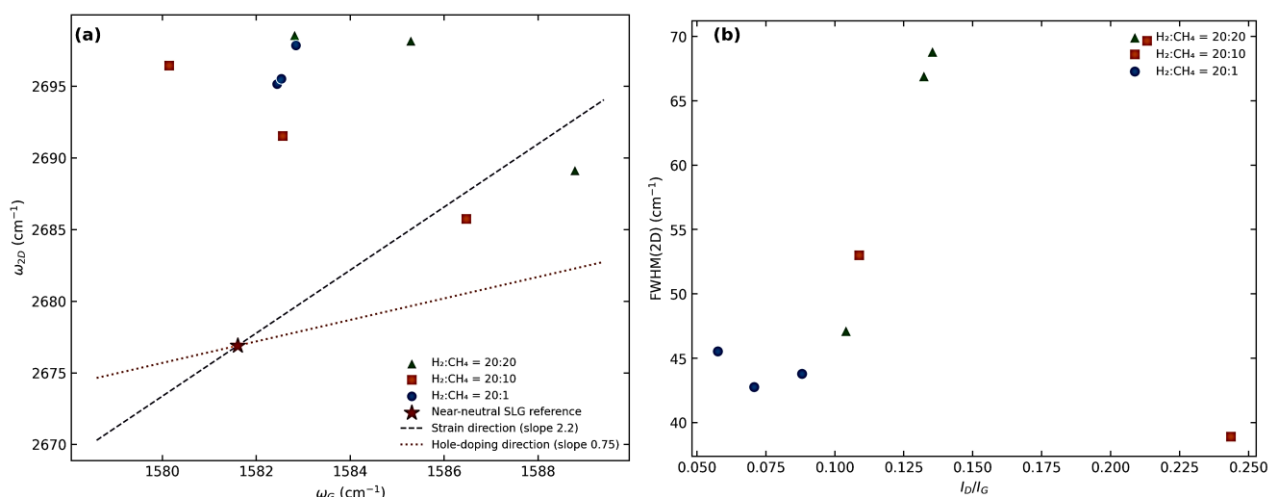


Fig. 3. Raman correlation plots for nine spectra: (a) ω_G – ω_{2D} positions with qualitative strain and hole-doping directions [8]; (b) I_D/I_G versus FWHM(2D)

3.5. Effect of methane supply. With temperature, H_2 flow, pressure and time fixed, lowering CH_4 from 20 to 1 sccm reduced the nominal carbon feed twentyfold. Graphene growth on Cu depends on methane activation, nucleation, lateral coalescence and hydrogen-assisted removal of weakly bound carbon [1–4]. The 20:1 response is consistent with suppression of excessive carbon supply, secondary nucleation and local multilayer overlap; the broader 20:10 and 20:20 distributions indicate less uniform competition among growth and etching processes. XRD identifies the common Cu-texture evolution, whereas methane flow differentiates the Raman response.

4. Conclusions. At a fixed growth temperature of 1020 °C, reducing CH_4 flow to 1 sccm at 20 sccm H_2 produced the most reproducible Raman response. For $H_2:CH_4 = 20:1$, $I_D/I_G = 0.072 \pm 0.015$,

$I_{2D}/I_G = 1.809 \pm 0.076$ and $FWHM(2D) = 44.03 \pm 1.41 \text{ cm}^{-1}$. Higher methane flows yielded substantially greater point-to-point variation. The combined weak D band, narrow 2D band and low dispersion support monolayer-like or thin few-layer graphene, without claiming complete monolayer coverage. The common thermal cycle strengthened Cu(200)-dominated texture without a significant lattice change or detectable bulk Cu oxide.

Acknowledgements. This work was supported by the Korea International Cooperation Agency (KOICA) through a joint project with the Korea Research Institute of Chemical Technology (KRICT) and the Center for Advanced Technologies (CAT), and within the budget-funded research activities of the Functional Materials Laboratory, CAT.

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3. Разработка и технология получения композиционных материалов

Негматова К.С. Технология флотационного обогащения медно-молибденовых руд с применением химических флотореагентов для извлечения медного концентрата	68
Xusenov A.Sh., Orazova Sh.Sh., Zokirov B.U., Kiyamova M.I., Raxmanberdiev G. Seritsin va inulin asosida kompozitsion plyonka olish va uning fizik-kimyoviy xossalari o'rganish	72
Саидова Ш.З., Каттаев Н.Т., Колядин В.Г., Акбаров Х.И. Синтез и характеристика гранулированного тройного сополимера 1-винилимидазола, акрилонитрила и дивинилбензола	75
Maxkamov B.G'. Vermikulit asosida olingan kompozitsion materialda benzol va suv bug'i adsorbsiyasi	79
Эшанкулова Г.Р., Ахмадов У.А. Тургунов Ф.Ф., Хасанов А.С. Ер остида танлаб эритиш усули билан уран қазиб олишда ҳосил бўладиган маҳсулдор эритмалардаги водород сульфидни фаолсизлантиришнинг самарали усулини ишлаб чиқиш	82
Bakhromova I.A., Vokhidova N.R. Synthesis of iron-modified chitosan for the purification of hydrogen sulfide waste from the oil and gas industry	85
Туляганова В.С. Разработка и исследование свойств композиционных кордиеритовых электрокерамических материалов на основе местного и вторичного сырья	87
Tursunkulov O.M., Gulyamov B.B., Sobitov M.A., Abduqahhorov F.I., Toxtabayev E.R., Uzakbergenov N.J., Bozorov S.S., Khojiev Sh.G. Effect of methane flow rate on the Raman characteristics and spatial uniformity of CVD graphene grown on high-purity copper at 1020 °C	91
Davlatova Z.Z., Safarov A.R., Abdiyeva F.I., Ixtiyarova G.A. <i>Apis mellifera</i> xitozani asosida suyuq neft tarkibidagi molibden va reniyni ajratib olish texnologiyasi	94
Очилов Э.А., Сайфиева П.О., Хамдамов Д.Х., Камолов Т.О. Способы переработки золы от сжигания энергетических углей	97

4. Прикладные, экономические и экологические аспекты применения композиционных материалов

Азимова Ш.А., Азимов Д.М. Перспективы вторичной переработки органических компонентов отходов щелочной очистки пирогаза	100
Sultanova N.S., Ismailova R.M., Ulliboboev A.M., Ismailov R.I. Tsellyuloza materiallarini olovga chidamli materiallarga aylantirish uchun vermikulit asosidagi olovga chidamli kompozitsiyaning tarkibini optimallashtirish	104
Шомуротов Ш.А., Содикова М.А., Абдурахмонов Ж.А., Ахмедов О.Р., Тураев А.С., Юлдашев Ж.М., Олимжонов Ж.У. Периодатное окисление декстрана и синтез оксимных производных путём нуклеофильного присоединения гидроксилamina	106
Razzoqov H.Q., Amonov M.R. Modifikatsiyalangan shofirkon bentoniti asosidagi kompozitsion sorbentlar va koagulyatsion tizimlar yordamida sanoat oqova suvlarini kompleks tozalash	110
Бозоров А.Н. Техногенные отходы предприятий металлургической отрасли и разработка технологии их переработки	112
Xokimov A.E., Eminov A.M., Kadirova Z.R., Xamdamova Sh.Sh. Sho'rsuv gilining mineralogik tarkibi va texnologik xususiyatlarini kompleks tadqiq etish	116
Nuriddinova G.A., Jalilov Sh.N. KMS va PAA ishtirokida melamin va gossipol bilan modifikatsiyalangan mochevina-formaldegid asosidagi yelimlovchi-bog'lovchining strukturaviy va termik xususiyatlari	120
Туляганова М.А., Маткаримов С.Т. Сравнительная оценка технологических схем извлечения технического теллура из медьэлектролитных шламов	124
Шомуротов Ш.А., Ахмедов О.Р., Тураев А.С., Юлдашев Ж.М., Олимжонов Ж.У., Туляшева М.А., Тураева Х.К. Восстановление оксимных производных декстрана и получение аминированного полисахарида	127
Амонова Н.М., Темиров Ў.Ш., Жўраев И.И. Оқова сув чўкиндиларини компостлашда органик моддалар, азот ва гумус моддаларининг ўзгариши	131
Очилов Э.А., Сайфиева П.О., Хамдамов Д.Х., Камолов Т.О. Исследование процесса извлечения скандия из зольных техногенных отходов с применением ионообменного сорбента	133