A New Generation of Nanotechnological Product and Process

Large-Area Synthesis of High-Quality and Controllable Thickness Graphene Films by Rapid Thermal Annealing

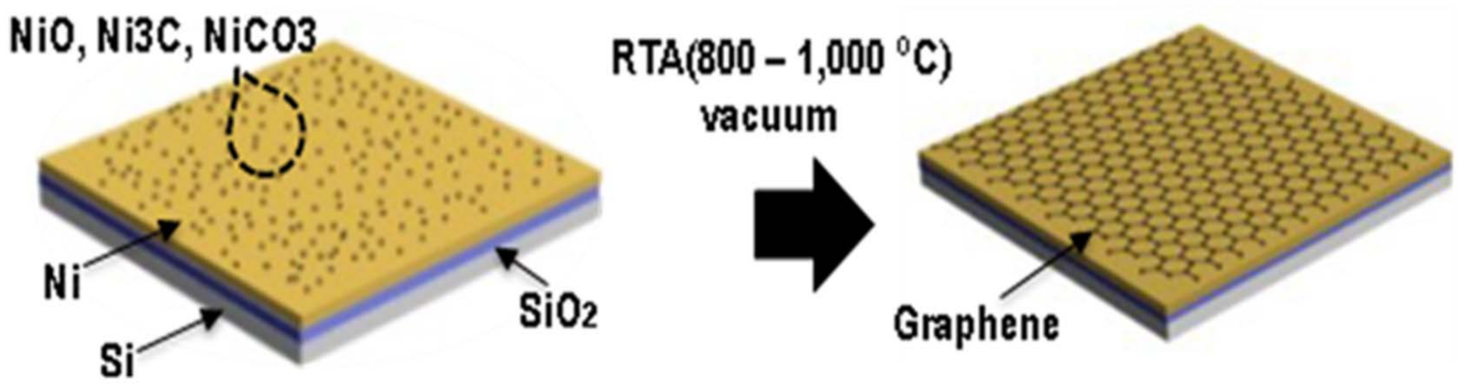
Ph.D Candidate
: Jae Hwan Chu

School of Mechanical and Advanced Materials Engineering, Ulsan National Institute of Science and Technology

UNIST
Ulsan National Institute of Science and Technology

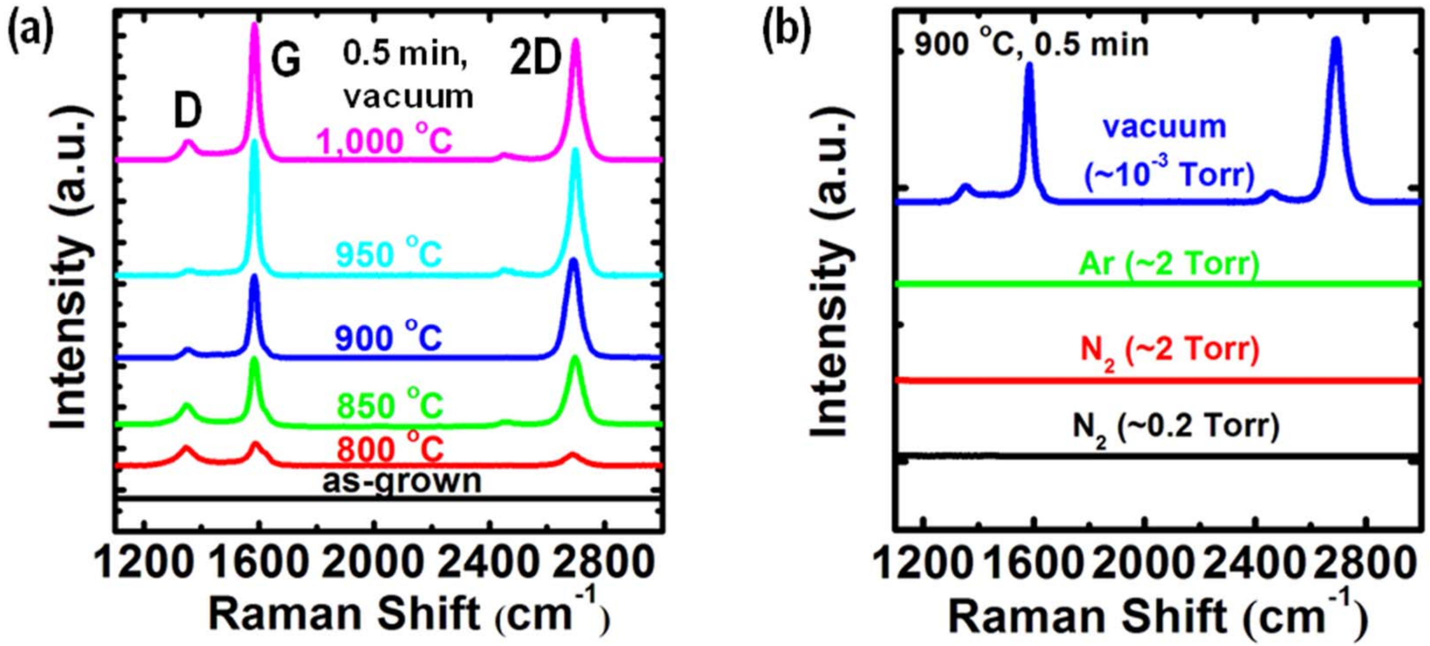
Rapid Thermal Annealing (RTA)

- **Nickel – assisted graphene growth using RTA**



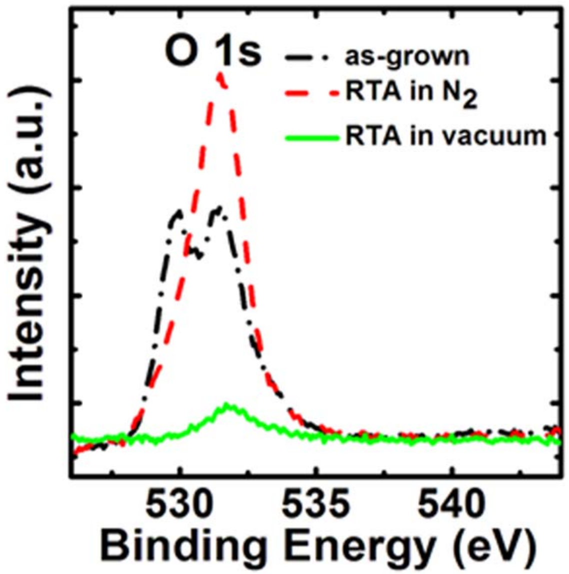
- **Spontaneous formation , Carbon- and oxygen-containing compounds**
- **Few-layer graphene films were formed on a nickel surface**

Rapid Thermal Annealing (RTA)
-Temperature (800 ~ 1000℃) & Various ambient



- Few-layer graphene films are formed under vacuum (~10-3 Torr) at temp. ranging from 800 ℃ and 1000 ℃ for 0.5 – 4min
- No graphene form when inert gases are introduced during the RTA process

Growth mechanism



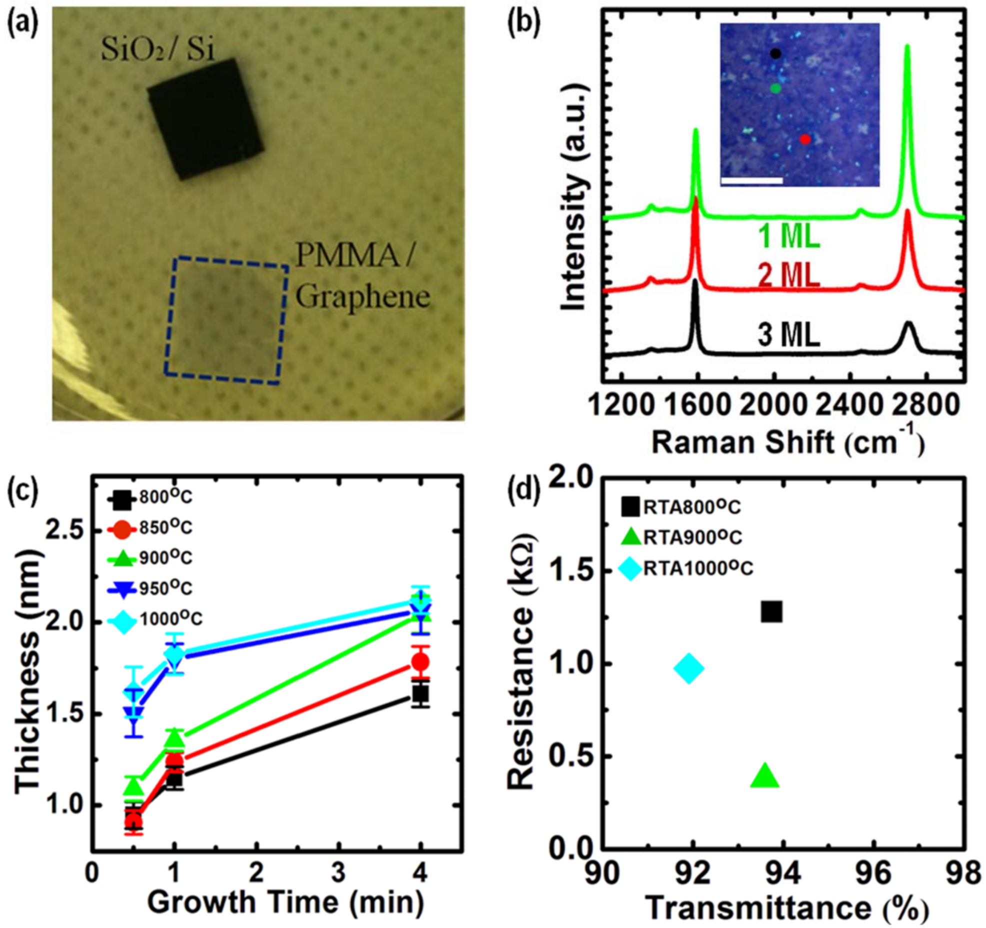
- **Dominant factor – oxygen evaporation rate**

  1) Inert gas - RTA
  No significant change in oxygen concentration
  → **No graphene form**

  2) Vacuum – RTA
  Graphene forms in all investigated temperature, along with oxygen evaporation from surface

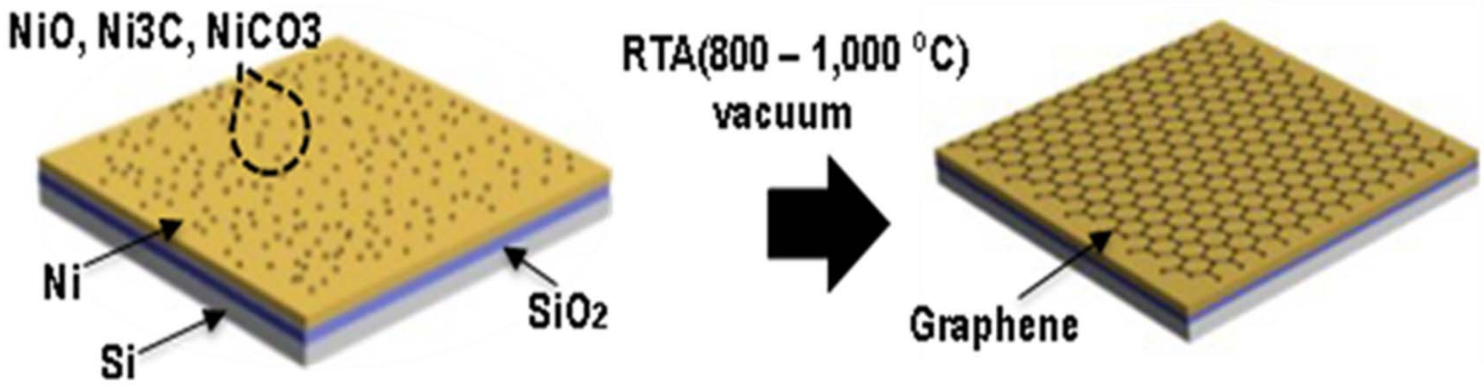
• Presence of Ar or N_2 during RTA may lead to a much reduced oxygen evaporation rate
→ The oxygen atoms desorbing from the surface have a finite probability of being reflected back to the nickel surface by collision with Ar or N_2, as pointed out <u>by Langmuir and Fonda</u>. **(Phys. Rev. 43, 401 (1912), (Phys. Rev. 31 (260))**

Characterization of graphene at RTA-vacuum



The thickness and physical properties of the graphene layers are strongly dependent on the RTA temperature and time.

Conclusion



• The *merits* of our method are as follows.

1) Simply grown by annealing the nickel films at high temperature under vacuum

2) The consuming time of process is highly short

3) The thickness of graphene layers is controlled by RTA temperature and time

4) comparable structural and optoelectronic qualities with CVD- graphene

THANK YOU

ACS Appled Materials & Interface 4(3): 1777 (2012)

Any other questions?

ACS APPLIED MATERIALS & INTERFACES

Research Article

www.acsami.org

Facile Synthesis of Few-Layer Graphene with a Controllable Thickness Using Rapid Thermal Annealing

Jae Hwan Chu,[†] Jinsung Kwak,[†] Tae-Yang Kwon,[†] Soon-Dong Park,[†] Heungseok Go,[‡] Sung Youb Kim,[†,§] Kibog Park,[‡] Seoktae Kang,[∇] and Soon-Yong Kwon*[,†,‡,§]

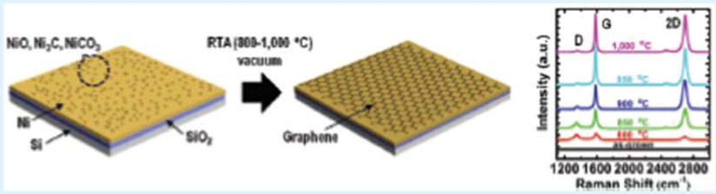
[†]School of Mechanical and Advanced Materials Engineering, Ulsan National Institute of Science and Technology, Ulsan 689-798, Republic of Korea

[‡]School of Electrical and Computer Engineering, Ulsan National Institute of Science and Technology, Ulsan 689-798, Republic of Korea

[§]Low Dimensional Carbon Materials Center, Ulsan National Institute of Science and Technology, Ulsan 689-798, Republic of Korea

[∇]Department of Civil Engineering, Kyung Hee University, Yongin 446-701, Republic of Korea

ABSTRACT: Few-layer graphene films with a controllable thickness were grown on a nickel surface by rapid thermal annealing (RTA) under vacuum. The instability of nickel films in air facilitates the spontaneous formation of ultrathin (<2−3 nm) carbon- and oxygen-containing compounds on a nickel surface; thus, the high-temperature annealing of the nickel samples without the introduction of intentional carbon-containing precursors results in the formation of graphene films. From annealing temperature and ambient studies during RTA, it was found that the evaporation of oxygen atoms from the surface is the dominant factor affecting the formation of graphene films. The thickness of the graphene layers is strongly dependent on the RTA temperature and time, and the resulting films have a limited thickness (<2 nm), even for an extended RTA time. The transferred films have a low sheet resistance of ~0.9 ± 0.4 kΩ/sq, with ~94% ± 2% optical transparency, making them useful for applications as flexible transparent conductors.



KEYWORDS: *graphene, rapid thermal annealing (RTA), few-layer, nickel, crystallization, transparent conductor*

Supporting information

Supporting Information

Experiments (RTA method)

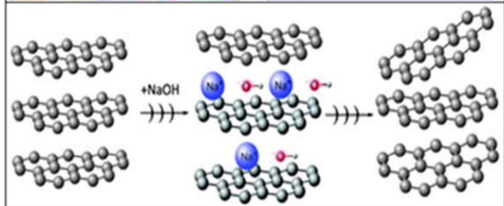
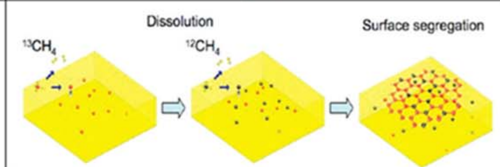
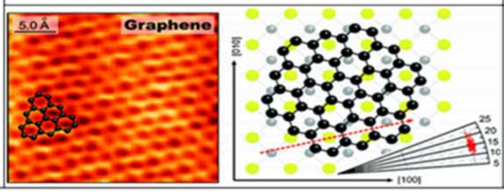
- The nickel films
  - Deposited in commercial evaporators (~10^{-6}-10^{-7} Torr) with solid Ni(99.99%)
  - Thickness of ~ 100nm deposited on a SiO2(300nm)/Si(100) substrate
  - The source and stored under atmosphere for a typical period of a few days.

- RTA(Rapid Thermal Annealing)
  - Temperatures ranging from 800 ºC to 1,000 ºC for 0.5 - 4 min
  - Vacuum (~10^{-3} Torr)
  - In inert gas (Ar, N_2) ambient (~0.2-2.0 Torr)

- How to employ the source of carbon
  - Trace amounts of unintentionally introduced carbon and oxygen atoms after Ni deposition

How to make graphene?

Table 1. Comparison of different methods for graphene production

	Schematic	Methods	Pros. & Cons
Top Down		*Mechanical Exfoliation (scotch Tape)*	*• High quality graphene • only Lab. Scale*
		*Chemical Exfoliation (Graphite → Go → RGO) (Graphite → Graphene)*	*• Good dispersion in various solvent • Large Area processing • Good adhesion for composite • High Defect Density*
Bottom Up		*CVD (Chemical Vapor Deposition)*	*• Excellent electrical properties • Large area processing • Additional steps for composite*
		*Epitaxial Growth (SiC wafer)*	*• High quality graphene • only Lab. scale*

Rapid Thermal Annealing (RTA)

K. Novoselov, Nature 490, 192 (2012).

CVD method

- An attractive method
- large area graphene synthesis > 6inch
- good optical, electrical and mechanical properties
- **applying various applications**

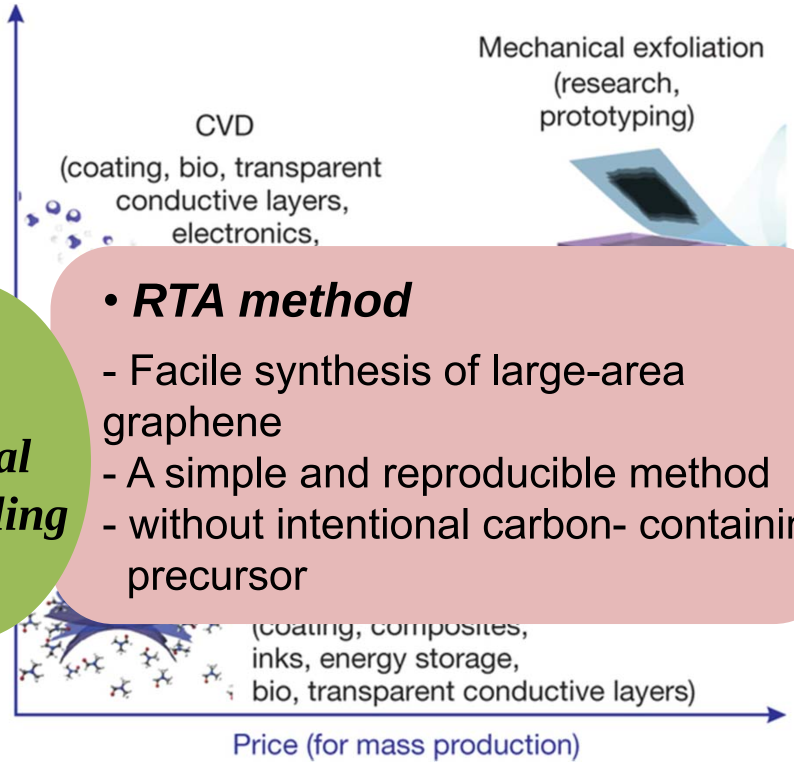
Why should the CVD method improved?

1) Required various parameters
2) Difficult control for growth.
3) Total process time is long.
4) Price.

Rapid Thermal Annealing

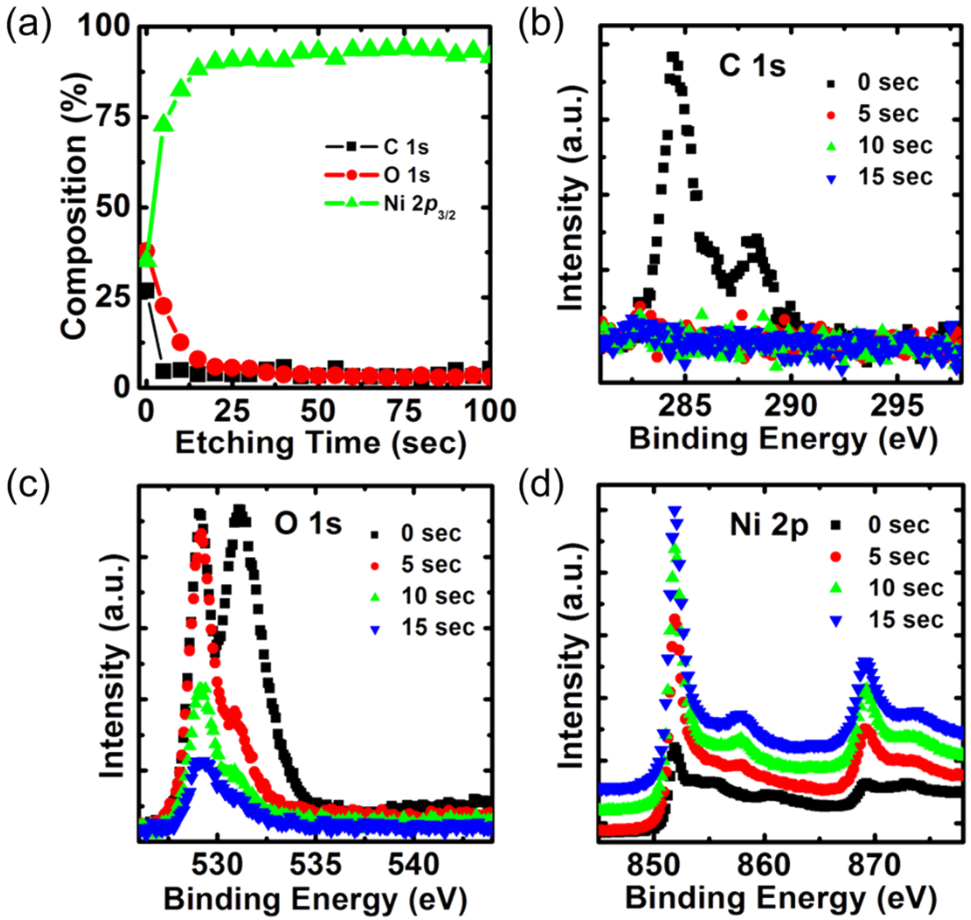
- ***RTA method***

- Facile synthesis of large-area graphene
- A simple and reproducible method
- without intentional carbon- containing precursor



How to employ the source of carbon

- XPS concentration-depth profile of Ni films before RTA process



- **The presence of Ultrathin Compounds on a Nickel Surface**

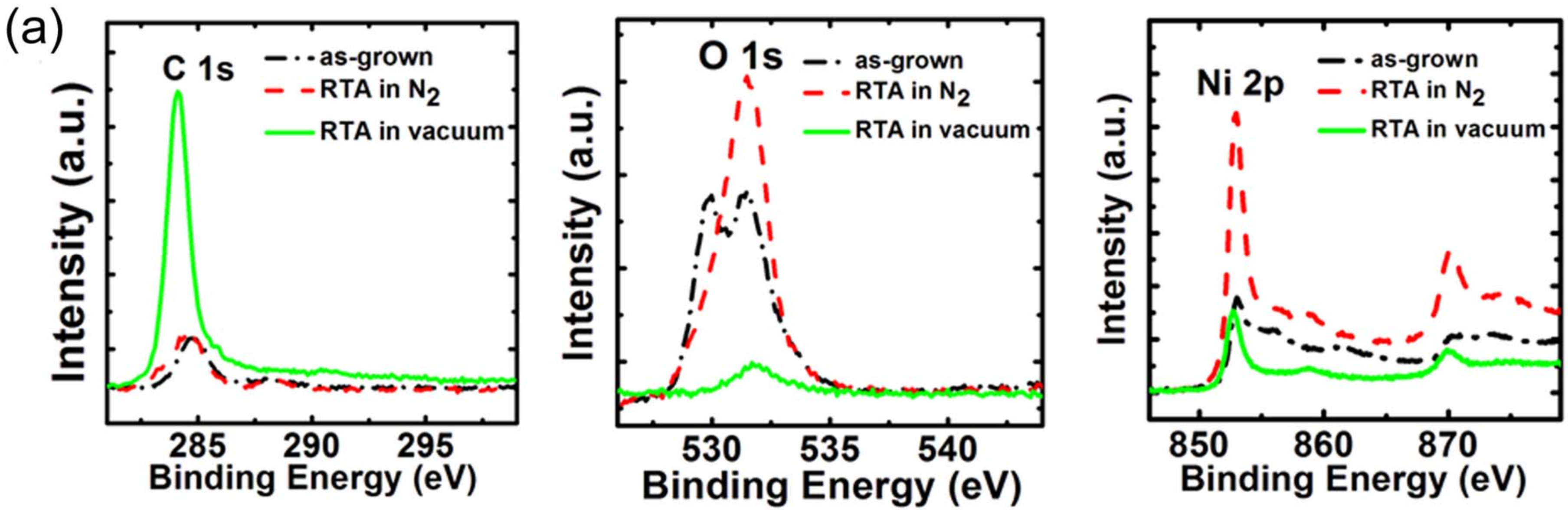
C 1s	Ni_3C	283.9 eV
	$NiCO_3$	288.4 eV
O 1s	NiO	529.7 eV
	$NiCO_3$	531.3 eV
Ni 2p	Ni_3C	852.9 eV
	NiO	853.8 eV
	$NiCO_3$	854.7 eV

UNIST
Ulsan National Institute of Science and Technology

Trace amounts of unintentionally introduced carbon and oxygen atoms after Ni deposition

WHAT MAKES DIFFERENCE GROWTH CONDITION?
- XPS CONCENTRATION PROFILE

- 1) As deposition, 2) RTA in N2 at 900℃ 1min , 3) RTA in vacuum at 900℃ 1min



- considerable compositional changes only vacuum ambient
- most oxygen atoms disappear after the vacuum – RTA process

What makes difference growth condition?
- XPS Depth profile

- 1) As deposition, 2) RTA in N2 at 900℃ 1min , 3) RTA in vacuum at 900℃ 1min

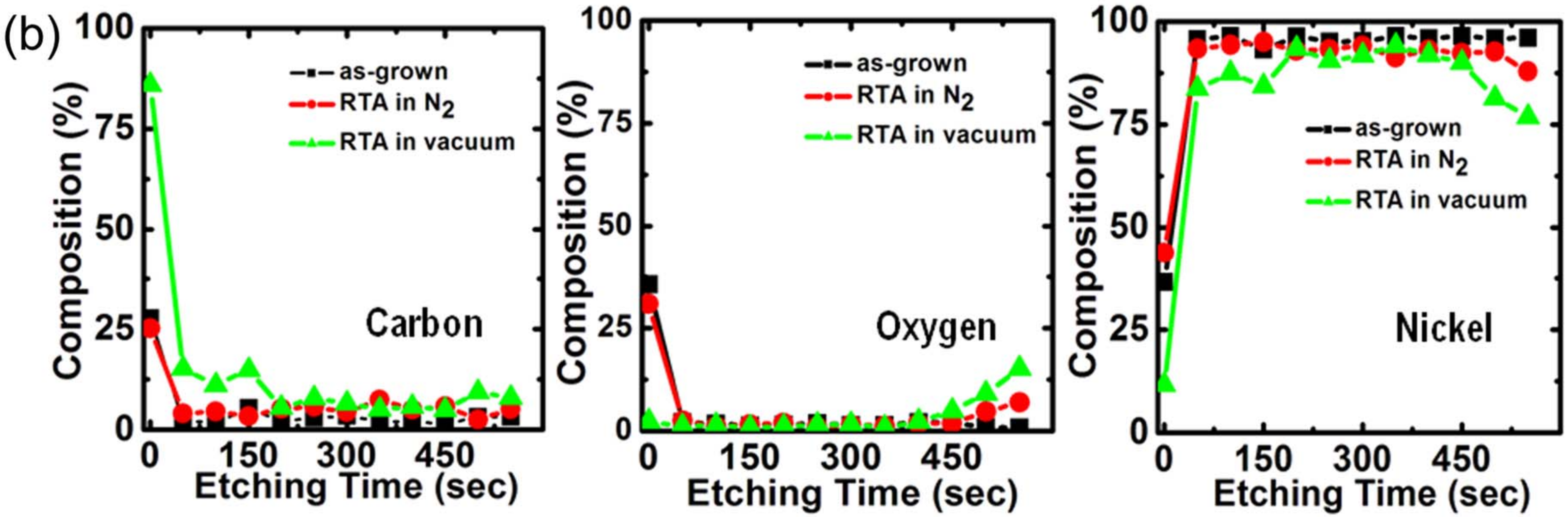


Table 4. the composition(%) of the top surface according to C1s and O1s

elements / Ambient	Carbon composition(%)	Oxygen composition(%)
As-grown	27.73%	35.68%
RTA in N2	25.26%	30.94%
RTA in vacuum	85.92%	2.36%