

2017년 진공기술 현장실무교육

최신 분석장치 산업현황 및 측정방법

2017. 6. 23

안재평

한국과학기술연구원 특성분석센터

1/120

목차



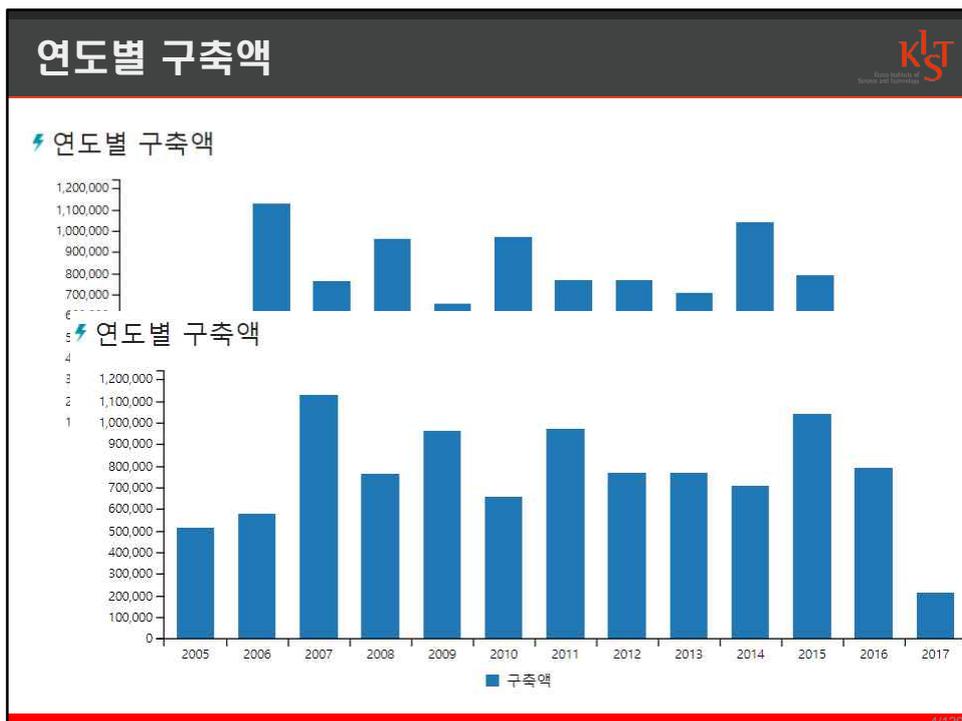
- 2017년 국가연구장비 현황
- 전자현미경 (SEM & TEM) 을 이용한 분석

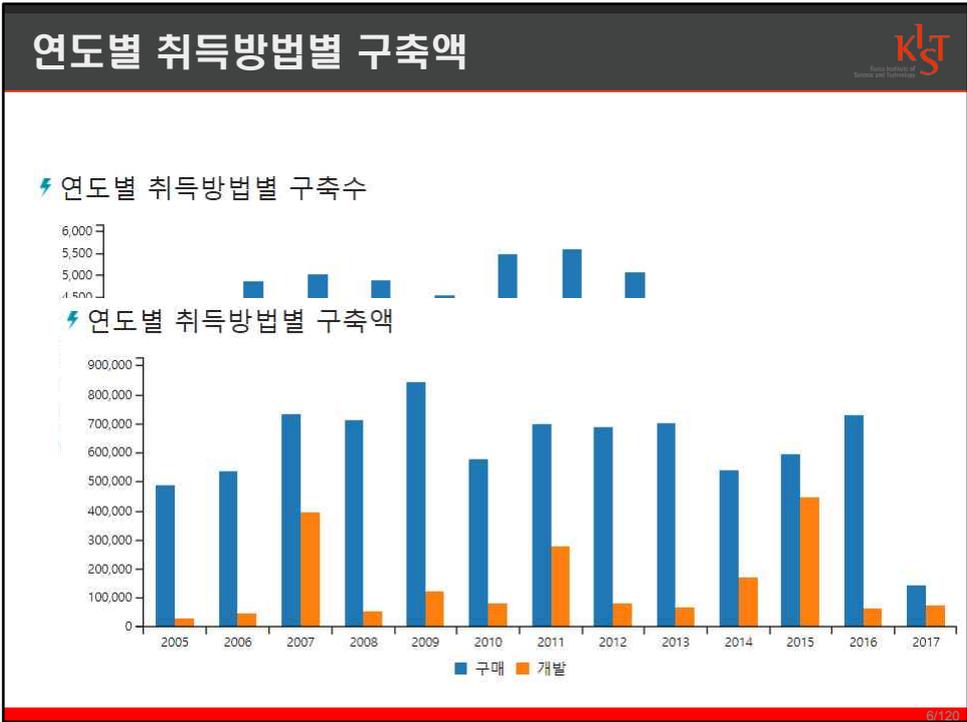
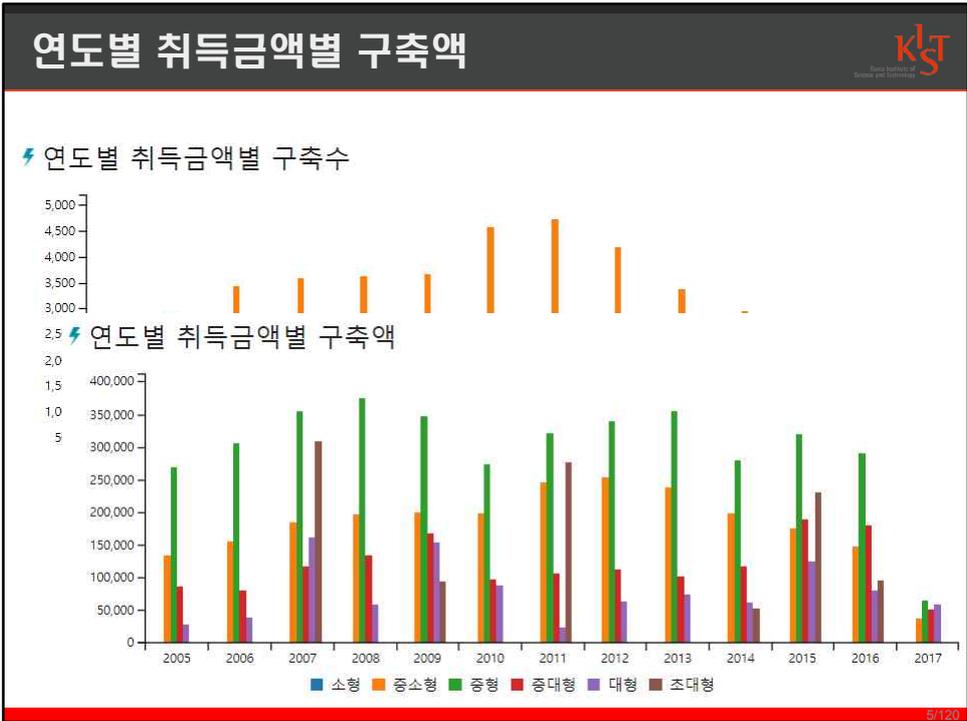
2/120

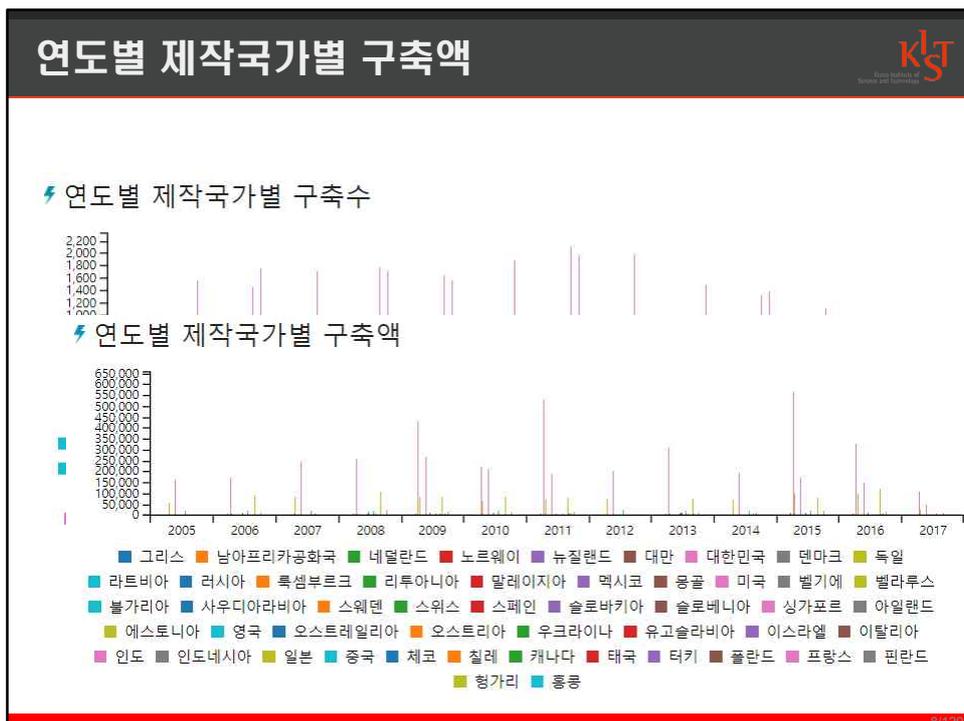
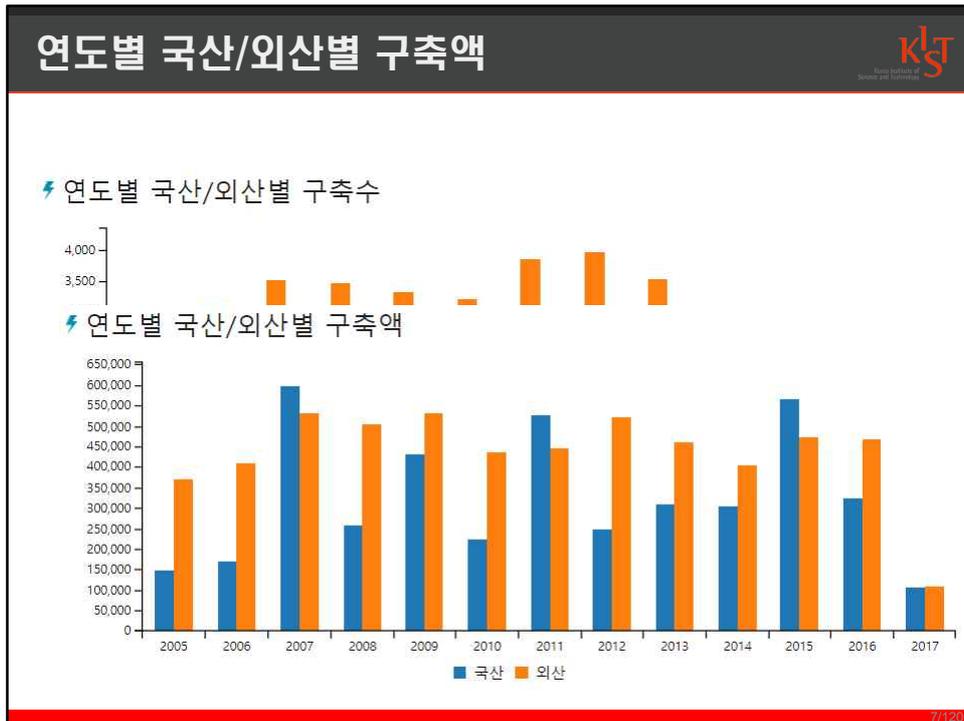

Korea Institute of Science and Technology

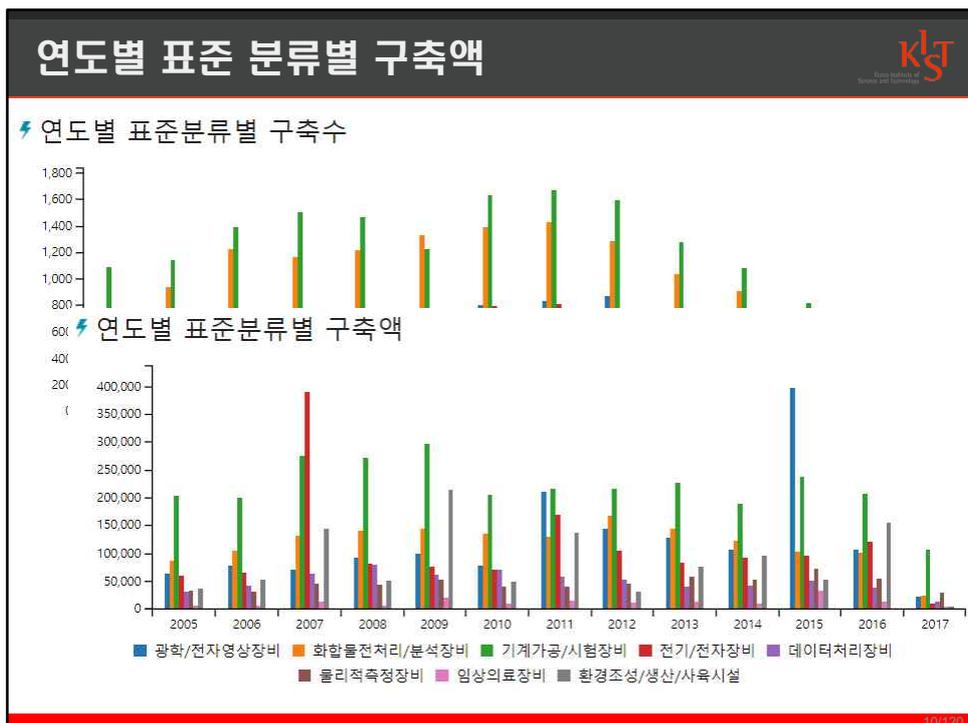
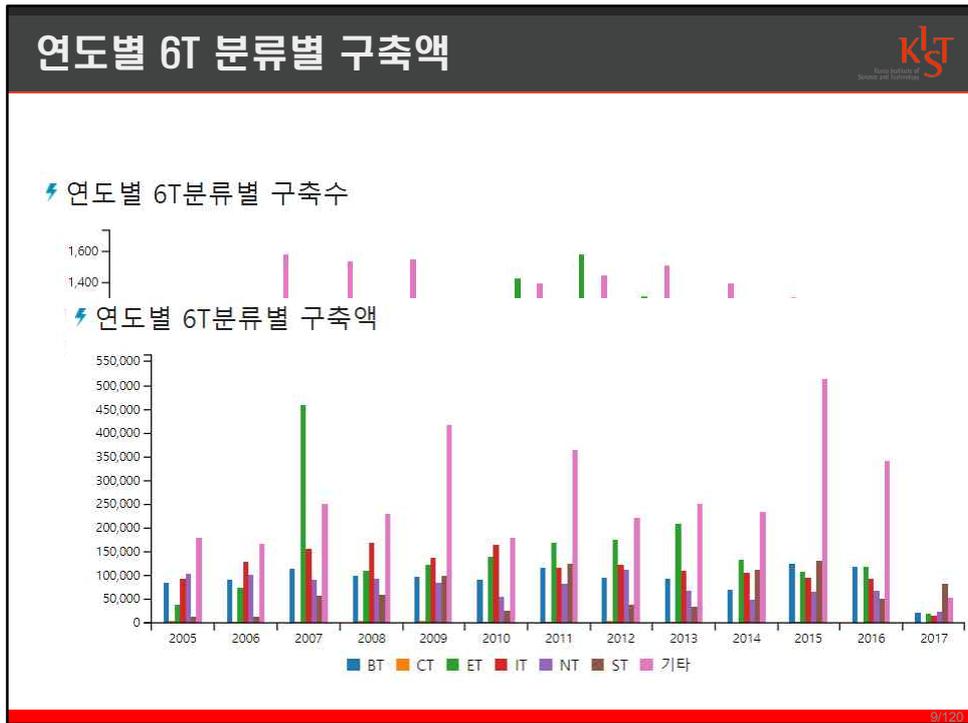
2017년 국가연구장비 현황

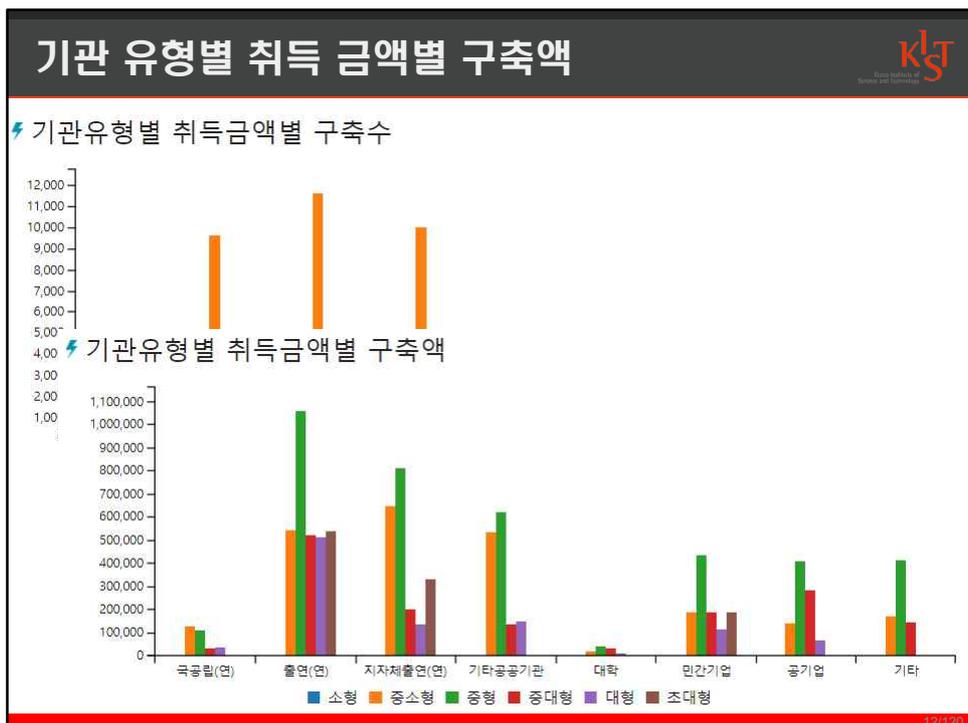
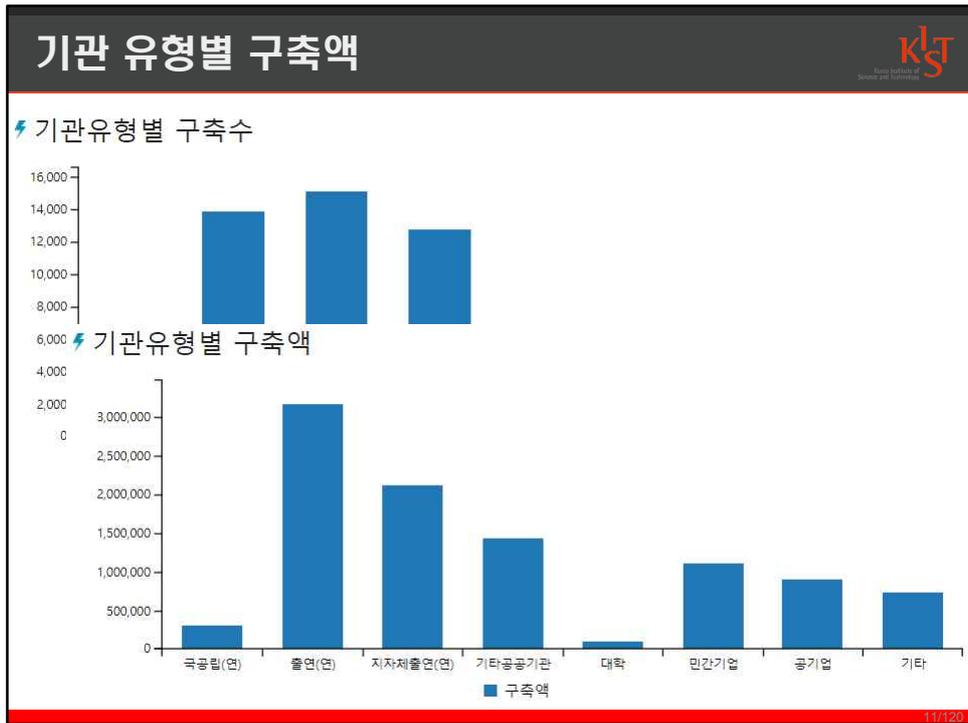
3/120

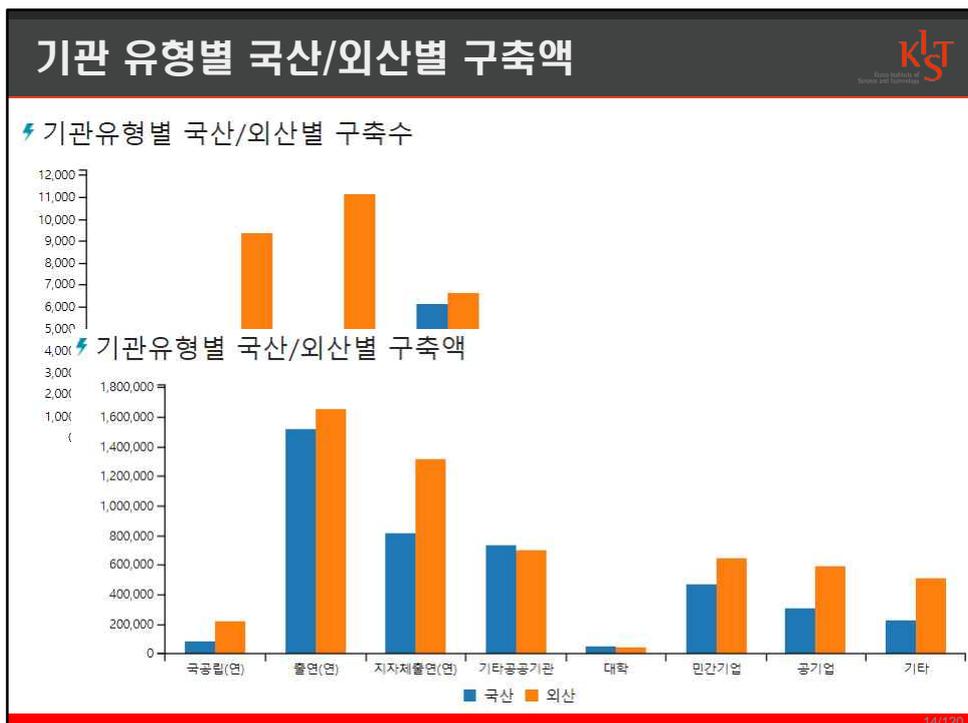
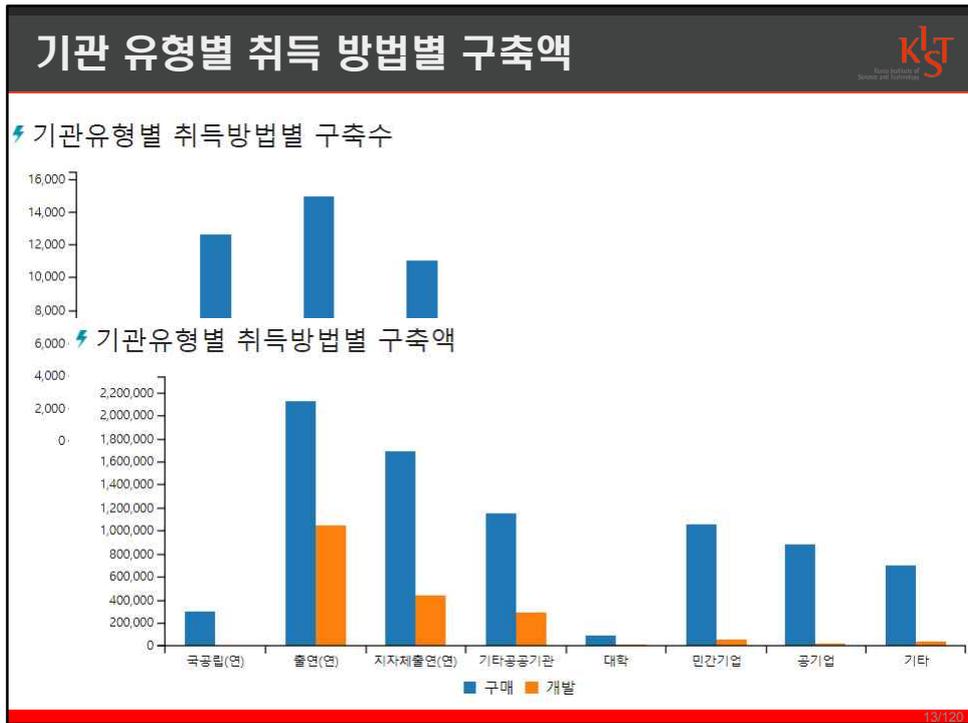


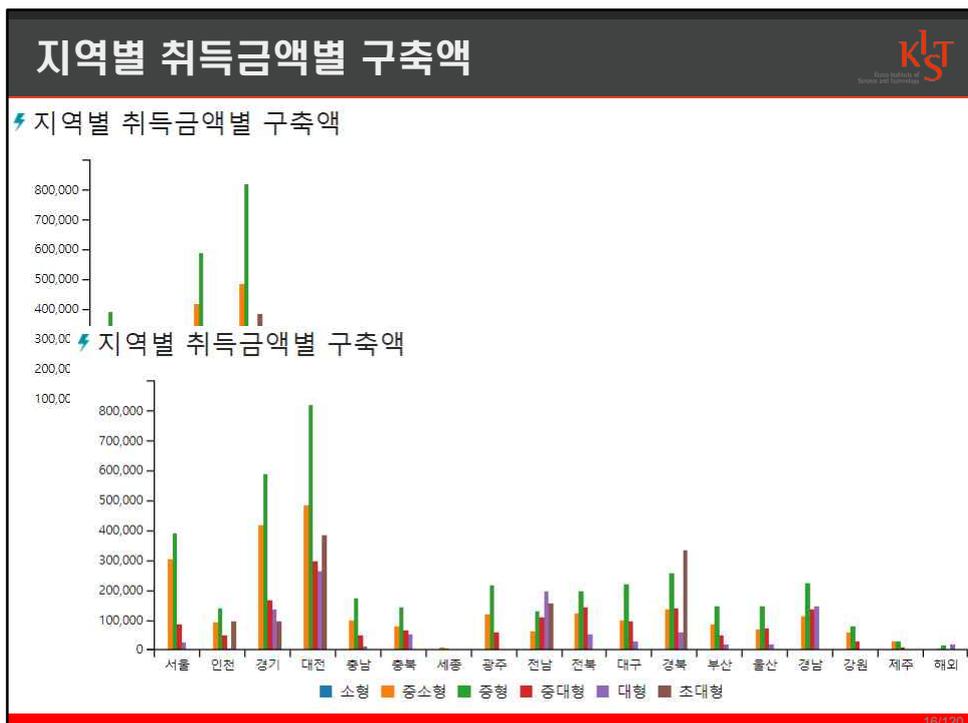
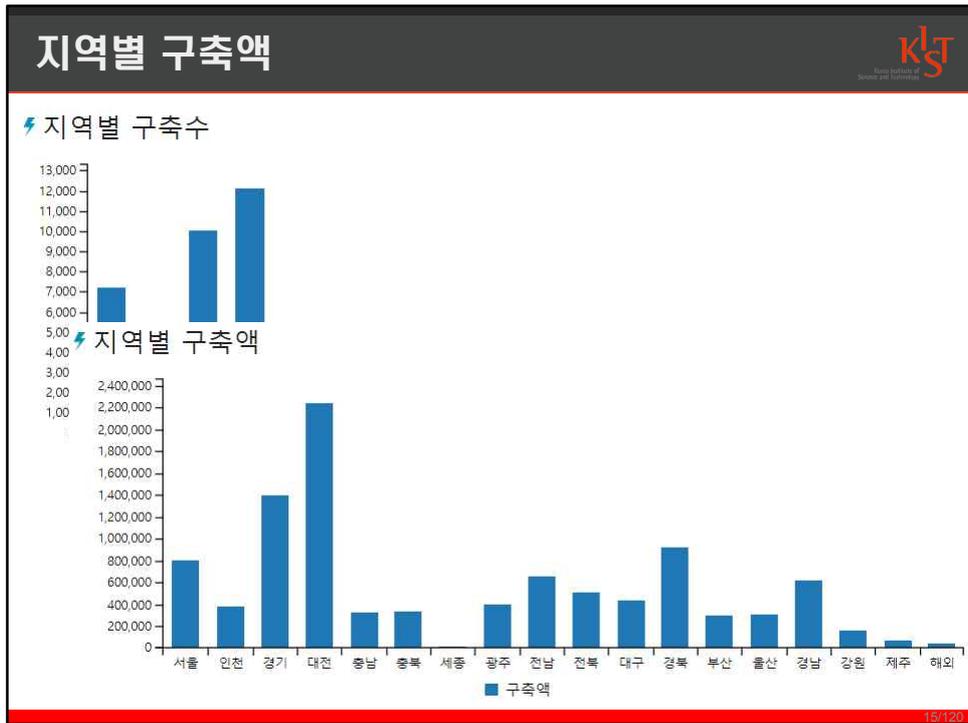


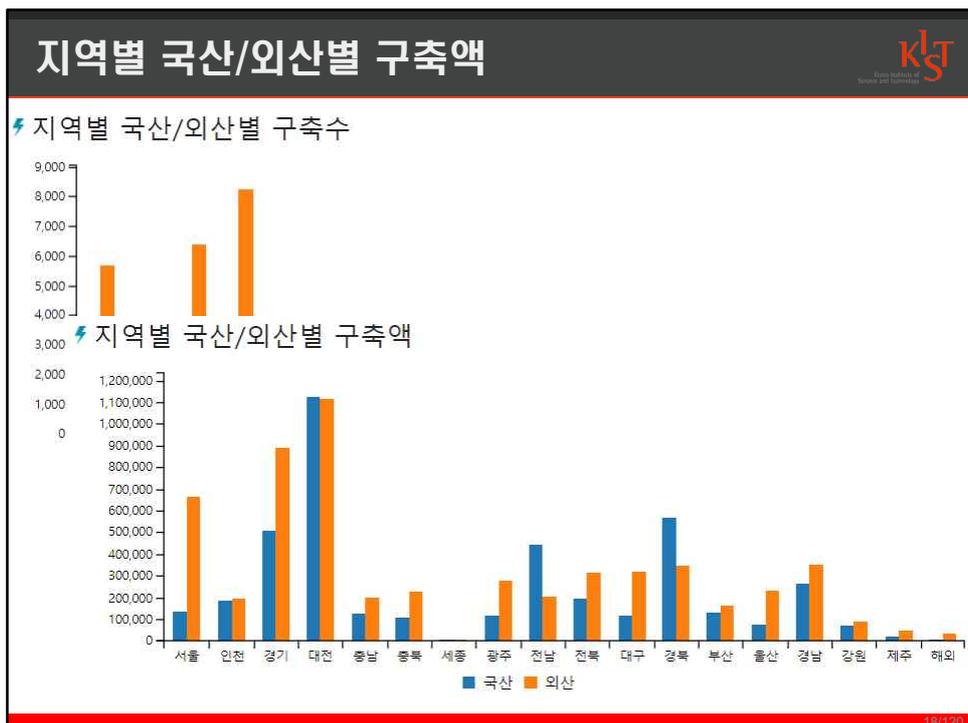
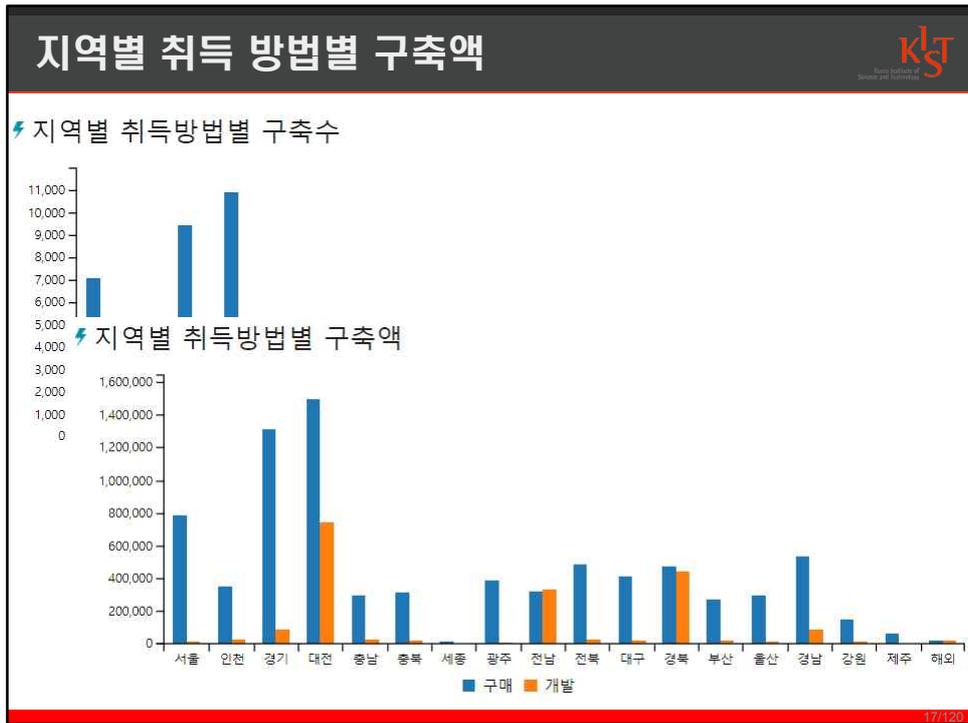


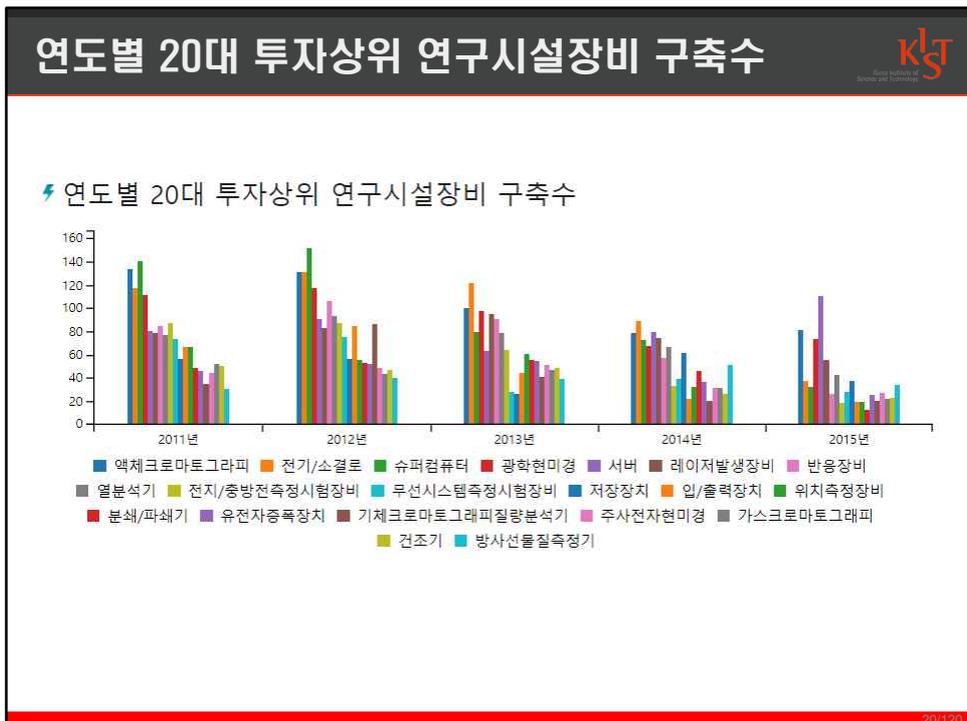
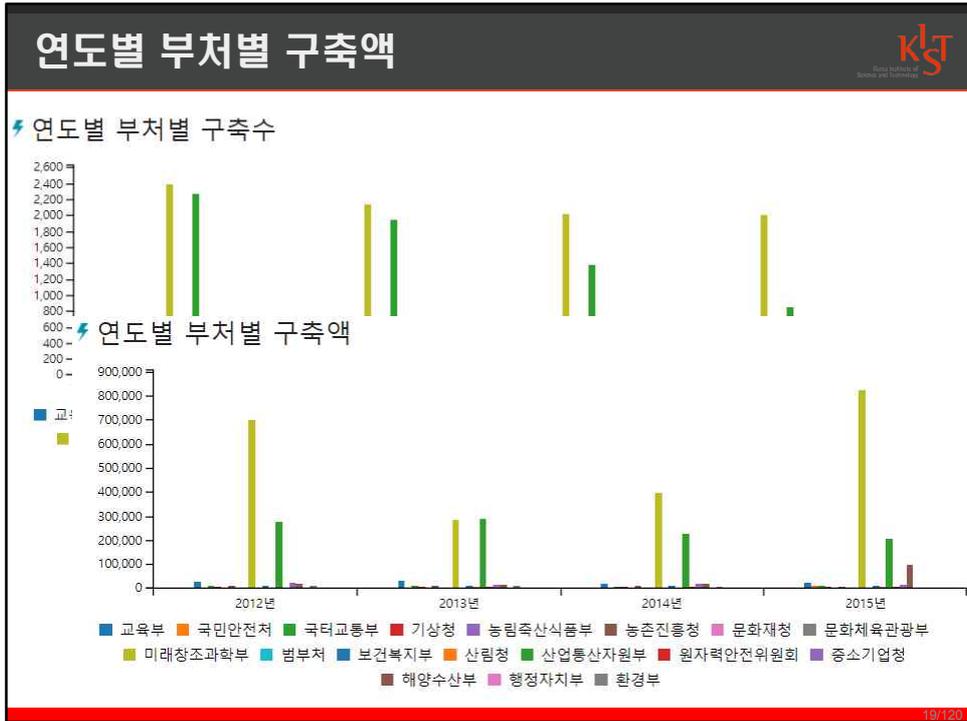


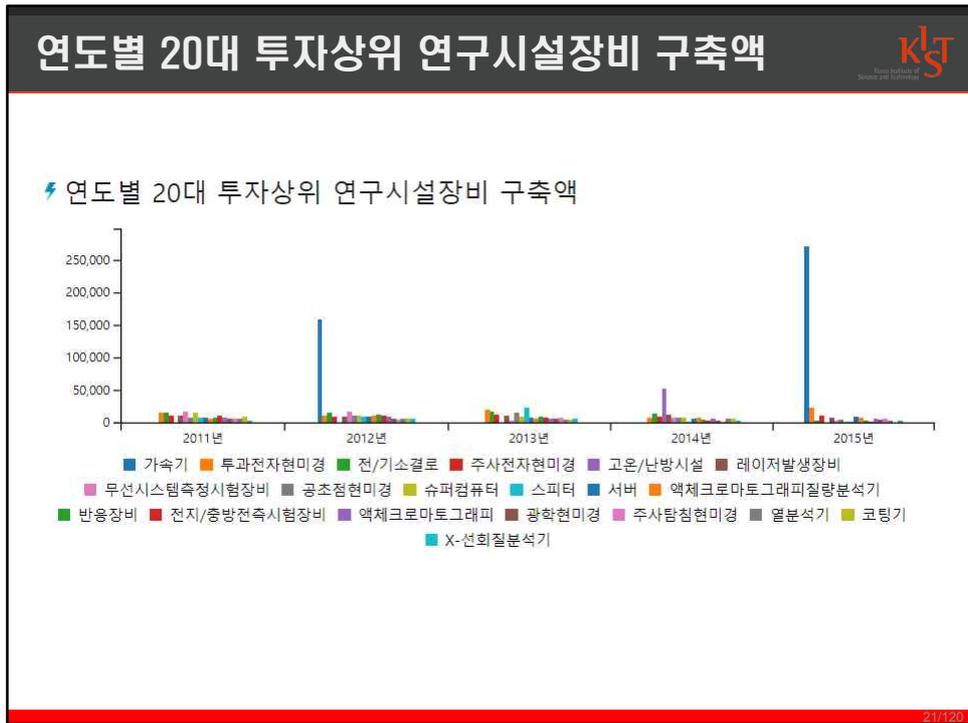












연도별 장비수



취득년도	장비구분	구매장비	개발장비	연구시설	Totals
2005		3,573	66	23	3,662
2006		4,038	60	22	4,120
2007		4,820	112	32	4,964
2008		4,986	152	29	5,167
2009		4,843	222	33	5,098
2010		4,507	308	39	4,854
2011		5,441	437	38	5,916
2012		5,540	487	46	6,073
2013		5,019	452	40	5,511
2014		4,001	418	48	4,467
2015		3,634	446	82	4,162
2016		3,104	241	109	3,454
2017		824	26	16	866
	Totals	54,330	3,427	557	58,314

22/120

 KIST
Korea Institute of Science and Technology

연도별 장비 구축액

취득년도	장비구분	구매장비	개발장비	연구시설	Totals
2005		480,694,562,254	28,214,871,628	7,054,017,033	515,963,450,915
2006		537,588,817,852	19,582,792,660	21,170,699,680	578,342,310,192
2007		704,003,482,751	382,159,125,692	41,118,012,803	1,127,280,621,246
2008		696,163,547,951	39,125,353,919	27,919,277,170	763,208,179,040
2009		736,972,996,509	48,747,918,573	175,375,395,042	961,096,310,124
2010		569,153,953,728	78,578,296,308	8,946,939,932	656,679,189,968
2011		691,541,165,003	269,191,657,828	10,699,286,575	971,432,109,406
2012		680,970,941,804	77,127,481,179	10,709,554,696	768,807,977,679
2013		696,368,580,754	65,037,018,599	5,882,372,778	767,287,972,131
2014		528,605,661,284	86,816,677,960	92,621,072,369	708,043,411,613
2015		580,360,338,645	415,321,150,604	43,074,293,983	1,038,755,783,232
2016		581,869,381,223	55,133,984,290	154,765,088,991	791,768,454,504
2017		136,970,262,704	70,396,621,225	4,757,773,403	212,124,657,332
	Totals	7,621,263,692,462	1,635,432,950,465	604,093,784,455	9,860,790,427,382

23/120

 KIST
Korea Institute of Science and Technology

우리는 왜 재료분석을 하는가?

24/120

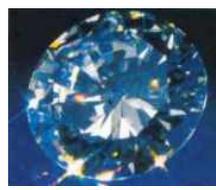
물질의 성질을 결정하는 최소단위는?

물(H_2O)은 수소분자(수소가스)의 성질도, 산소분자(산소가스)의 성질도 아닌 액체로서의 성질을 갖는다. 물을 수소가스와 산소가스로 분리하면 물의 성질은 사라진다.

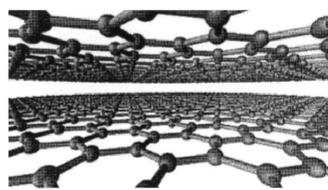
25/120

같은 원자도 결합형태가 달라진다면?

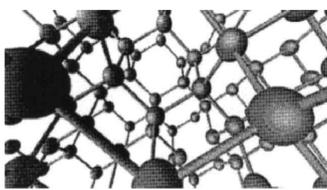




탄소원자로 이루어진 숯, 흑연, 다이아몬드가 서로 성질이 다른 것은 같은 탄소원자라도 결합하는 방법(결정구조)에 따라 성질이 달라지기 때문



흑연의 결정구조



다이아몬드의 결정구조

26/120

Key factors in Nanotechnology

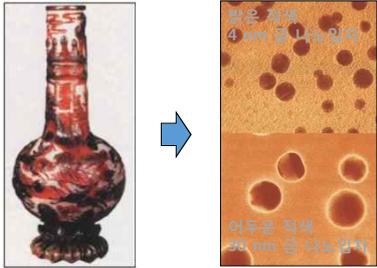


Enhanced surface properties : Catalysts, color

Roman Lycurgus cup (1600년 전)



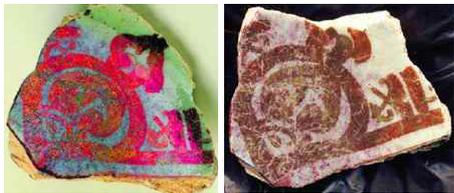
청나라 유리 (300년전)

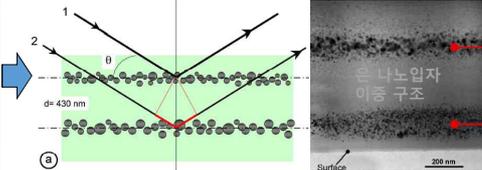


붉은 색상
4 nm 금 나노입자

어두운 적색
98 nm 금 나노입자

중세 도기 유약 (700년전)





금 나노입자 이중 구조

Surface 200 nm

27/120

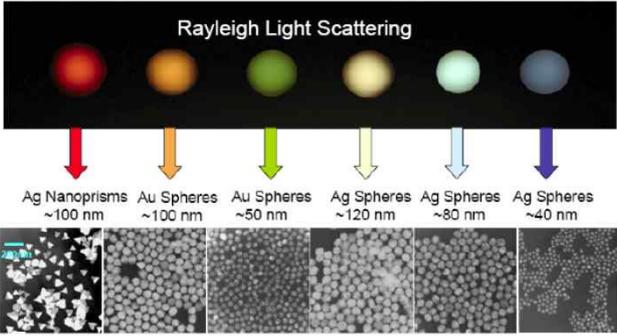
Key factors in Nanotechnology



Enhanced surface properties : Catalysts, color

Au / Ag Nanoparticles : TEM Observation

Rayleigh Light Scattering



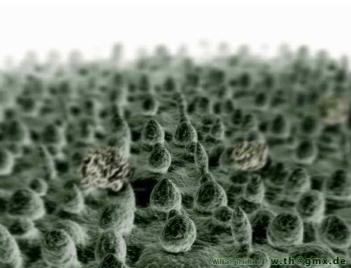
↓	↓	↓	↓	↓	↓
Ag Nanoprisms ~100 nm	Au Spheres ~100 nm	Au Spheres ~50 nm	Ag Spheres ~120 nm	Ag Spheres ~80 nm	Ag Spheres ~40 nm

Properties depend on particle size, shape and composition.

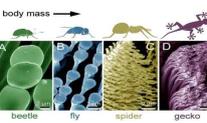
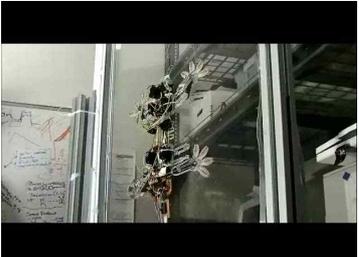
28/120

Characterization in Nanotechnology




관찰하기 - 따라하기 - 따라잡기

29/120

재료의 구조는 재료의 물성을 결정한다!!!



- 구조
 - 원자
 - 결정, 비정질
 - 화학구조 조성,
 - 형태, 크기, 복합화, 결합
- 이것이 왜 중요한가?
 - 기계, 전기, 화학, 광학, 자기, 열전, 촉매, 반응성
 - 물성을 결정하기 때문

30/120

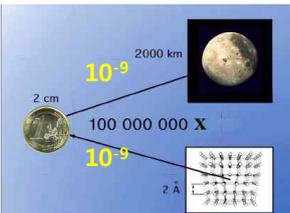

Korea Institute of Science and Technology

무엇을/어떻게 분석할 것인가?

31/120


Korea Institute of Science and Technology

Scale of things (Nanoscale)



2 cm 2000 km
 10^{-9}
100 000 000 X
 10^{-9}
2 Å

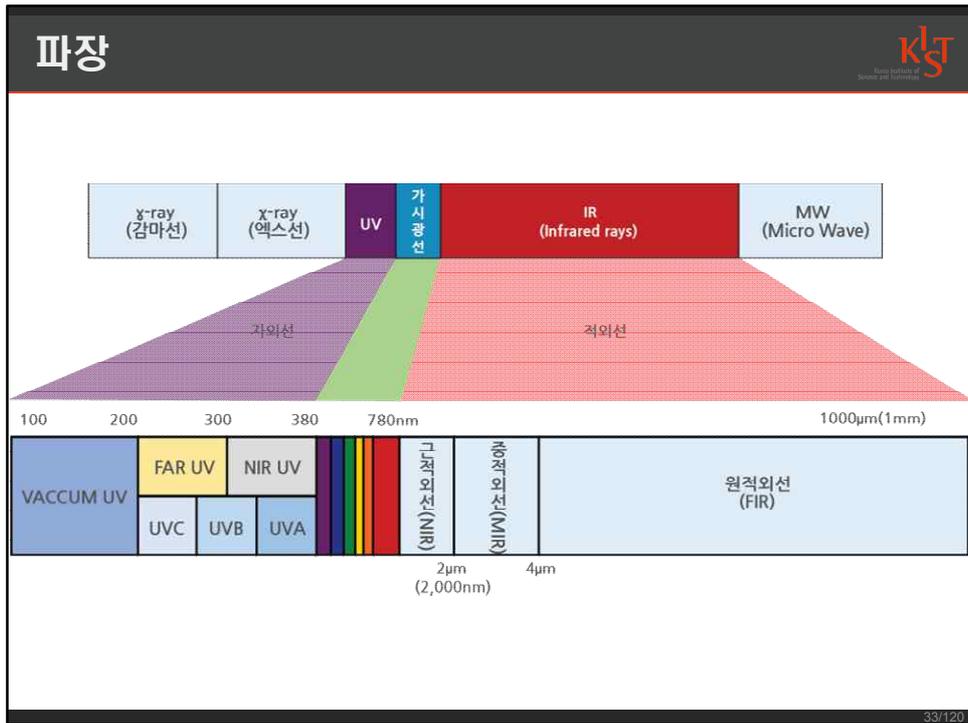


Earth from space

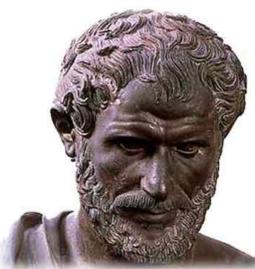


Nanostructure of Seashell

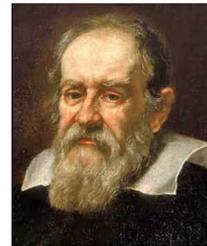
32/120



History of vacuum



Αριστοτέλης,
BC384-322



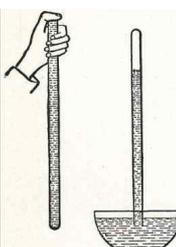
Galileo Galilei,
1564-1642



Evangelista Torricelli,
1608-1647



Blaise Pascal,
1623-1662



760 Torr
= 760 mmHg

1 Pa
 = 1 N/m² = 1 (kg·m/s²)/m² = 1 kg/m·s²
 = 0.01 mbar
 = 0.00001 bar
 = 7.5006 × 10⁻³ torr

진공내의 전자 운동

(1) 전기장 내의 전자 운동

- 전자가 B극판의 방향으로 받는 힘 : $F=eE=eV/d[N]=m_0\alpha[N]$
- 가속도 : $\alpha=eE/m_0=e/m_0\cdot V/d[m/s^2]$

[1] 초속도를 가지는 전자의 전기장 내에서의 운동

- ① $E[V/m]$ 의 평등 전기장 내에 있는 전자가 t 초 후의 속도
 $v_t=v_0+\alpha t[m/s]=v_0+eE/m_0t[m/s](\leftarrow\alpha=eE/m_0)$,
 v_0 : 초속도 $[m/s]$, α : 가속도 $[m/s^2]$

[2] 전자의 속도와 에너지

- ① B극판에 도착한 순간 전자의 속도 v_d
- ② 운동 에너지 $W=1/2m_0v_d^2=eV=1.602\times 10^{-19}V[J]$

[3] 전자 에너지의 단위

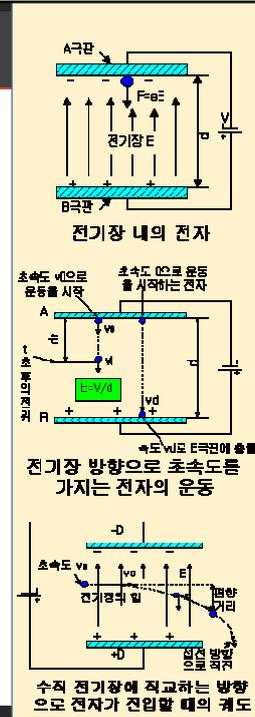
- ① 단위 : 1 전자 볼트 (1[eV]), 1[eV]= $1.602\times 10^{-19}[J]$

[4] 전자의 정전 편향

- ① 정전 편향 : 평등 전기장 $E[V/m]$ 중에 전기장과 직교하는 방향으로 초속도 $v_0[m/s]$ 의 전자가 진입되도록 하면, 전자에는 전기장에 의한 힘이 작용하여 양극(+)판 방향으로 진로가 구부러지면서 포물선으로 전자가 진행됨(자기장에 의하여 전자의 진로가 구부러지게 되는 것)

[5] 편향 거리

- 편향 거리는 편향 전압 V_d 에 비례



(2) 자기장 내의 전자 운동

<원 운동의 반지름과 각속도>

- ① 원운동의 구심력 : $F=BII=ev_0B$, 원심력: $m_0v_0^2/r$, $ev_0B=m_0v_0^2/r [N]$
- ② 원운동의 회전 각속도 : $\omega=v_0/r=eB/m_0[rad/s]$

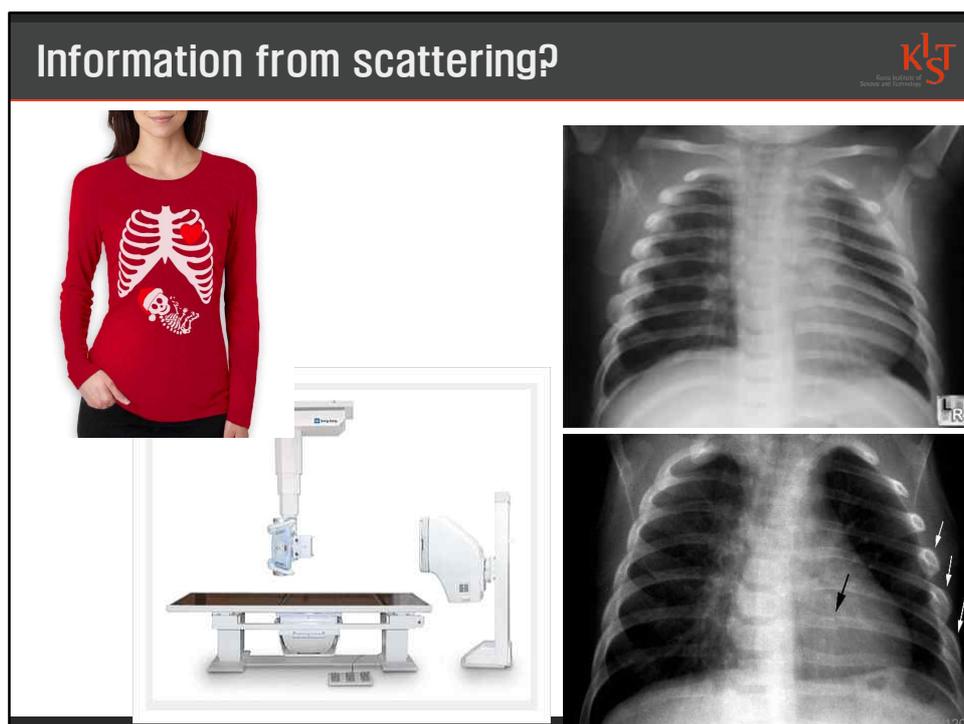
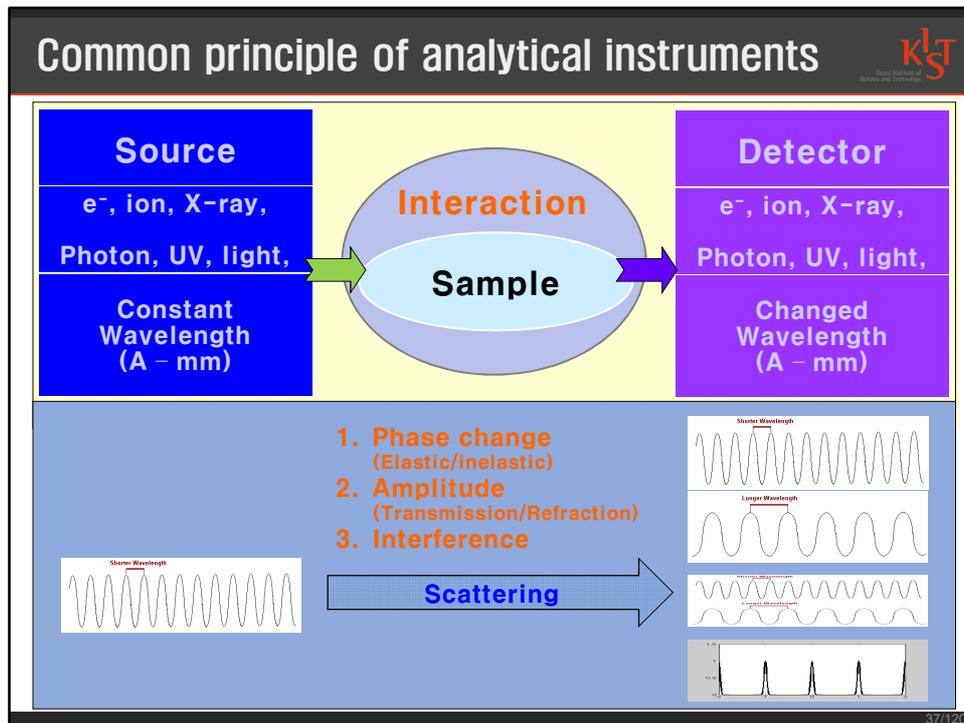
<나선 운동>

- ① v_0 의 자기 방향의 속도 $v_x=v_0\cos\theta[m/s]$
- ② v_0 의 수직 방향의 속도 $v_y=v_0\sin\theta[m/s]$

(3) 전자 빔

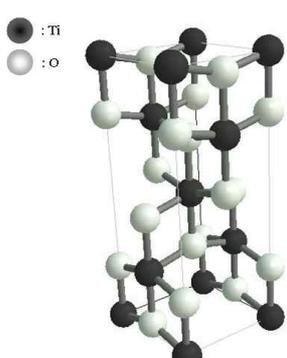
<전자 빔의 작용>

- (가) 형광 작용 : 황화 카드뮴(CdS), 아연(Zn) 등의 염기류에 구리(Cu)등의 불순물을 넣은 형광도료에 전자빔을 쬐면 발광.
- (나) 사진 작용 : 사진의 감광판에 전자 빔을 쬐어 현상하면, 빛을 비쳤을 때와 같이 감광되어 검게 됨.
- (다) X선 방사 : 고진공 내를 고속으로 운동하는 전자빔이 물질의 표면에 충돌해서 전지되면, 거기에서 극히 파장이 짧은($10^{-18}\sim 10^{-12}[m]$ 정도)전자기파 발생.
- (라) 열 작용 : 전자 빔이 물체에 충돌할 때, 그 운동 에너지는 열 에너지로 변함



International Table for Crystallography





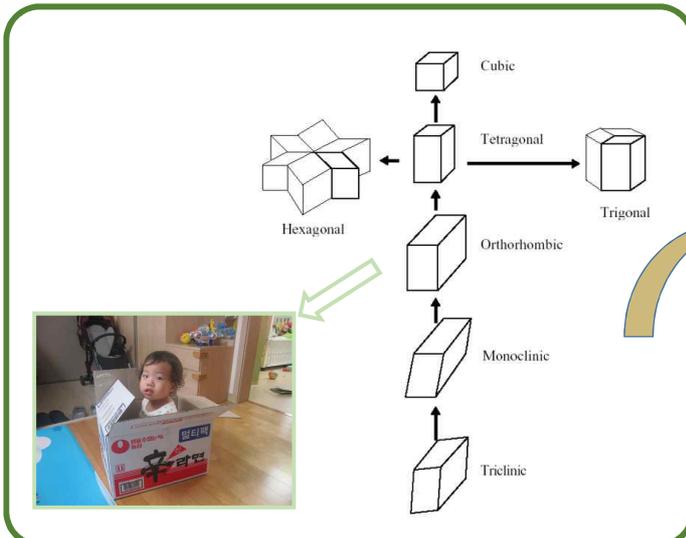
Ti atom	atom #	O atom	atom #	O atom	atom #
(0, 0, 0)	8	(0, 0, 0.2064)	4	(0.5, 0.5, 0.7064)	1
(0, 0.5, 0.25)	2	(0, 0.5, 0.4564)	2	(0.5, 0, 0.9564)	2
(0.5, 0.5, 0.5)	1	(0, 0.5, 0.5436)	2	(0.5, 0, 0.0436)	2
(0.5, 0, 0.75)	2	(0.5, 0.5, 0.2936)	1	(0, 0, 0.7936)	4

31개의 원자를 포함하고 있는 TiO₂ 단위셀

39/120

Symmetry of crystal system





Crystal system 7
Bravais lattice 14
Point group 32
Space group 230



단위격자의 길이와 각도에 따른 대칭성과 주기성의 변화

40/120

Bravais Lattice



Crystal systems	P	C	I	F
Triclinic				
Monoclinic				
Orthorhombic				
Trigonal				
Tetragonal				
Hexagonal				
Cubic				

7개의 결정구조와 14개의 Bravais lattice와의 관계

41/120

Common principle of analytical instruments



Source

e⁻, ion, X-ray,
Photon, UV, light,
Constant
Wavelength
(λ - nm)

Interaction

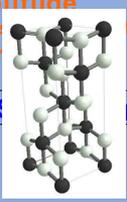
Sample

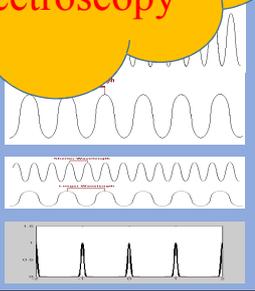
Detector

e⁻, ion, X-ray,

1. Image
2. Diffraction
3. Spectroscopy

1. Phase char
(Elastic/inelastic)
2. Amplitude
(Transmittance)
3. Inter





42/120

TEM과 물성


우리가 보고 싶은 것	TEM에서 할 수 있는 것
<ul style="list-style-type: none"> • 물리, 화학, 역학, 광학, 자성 • 미세조직 <ul style="list-style-type: none"> - 직접관찰 • 물리 <ul style="list-style-type: none"> - 원자결합형태 (밴드갭) • 화학 <ul style="list-style-type: none"> - 조성분석 - 화학결합계면 결합 • 역학 <ul style="list-style-type: none"> - 응력, 변형 • 혼합 <ul style="list-style-type: none"> - 계면 화학성분 이동 - 계면 변형량 • 결정학 <ul style="list-style-type: none"> - 결정성 - 방위 	<ul style="list-style-type: none"> • 이미지 형성 <ul style="list-style-type: none"> - 미세조직 - 비정질, 결정 - BF/DF - 석출물, 경계면 세우는 방법 • HRTEM의 형성원리 및 해석 방법 • STEM 이미지 (Z contrast) • 회절 형성 <ul style="list-style-type: none"> - SAD, Kikuchi, CBED, NED • 조성 분석 <ul style="list-style-type: none"> - EDS, EELS • 맵핑 <ul style="list-style-type: none"> - EDS, EFTEM

43/120



재료 분석장비들

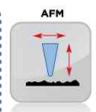
44/120

Nano-materials and analytic methods

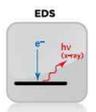




AES, Auger
Auger Electron Spectroscopy



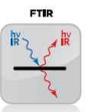
AFM
Atomic Force Microscopy



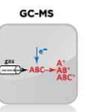
EDS
Energy Dispersive X-Ray Spectroscopy



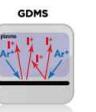
FIB
Focused Ion Beam Imaging



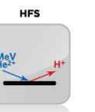
FTIR
Fourier Transform Infrared Spectroscopy



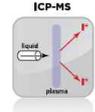
GC-MS
Gas Chromatography Mass Spectrometry



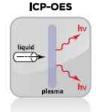
GDMS
Glow Discharge Mass Spectrometry



HFS
Hydrogen Forward Scattering Spectrometry



ICP-MS
Inductively Coupled Plasma Mass Spectrometry



ICP-OES
Inductively Coupled Plasma Optical Emission Spectrometry



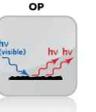
IGA
Instrumental Gas Analysis



LA-ICPMS
Laser Ablation Inductively Coupled Plasma Mass Spectrometry



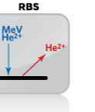
LEXES
Low Energy X-ray Emission Spectrometry



OP
Optical Profilometry



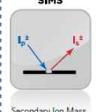
Raman
Raman Spectrometry



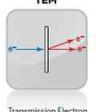
RBS
Rutherford Backscattering Spectrometry



SEM, EBSD, EBIC
Scanning Electron Microscopy
Electron Backscatter Diffraction
Electron Beam Induced Current



SIMS
Secondary Ion Mass Spectrometry



TEM
Transmission Electron Microscopy



TGA, DTA, DSC
Thermogravimetric Analysis
Differential Thermal Analysis
Differential Scanning Calorimetry



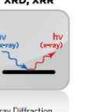
TOF-SIMS
Time-of-Flight Secondary Ion Mass Spectrometry



TXRF, XRF
Total Reflection X-ray Fluorescence
X-ray Fluorescence



XPS
X-Ray Photoelectron Spectrometry



XRD, XRR
X-Ray Diffraction
X-ray Reflectivity



www.eag.com/mc
Copyright ©2014 Evans Analytical Group - 10/14 88038

45/120

Various analytical techniques



Acronyms Glossary

This glossary lists all the acronyms referred to in the encyclopedia together with their meanings. The major technique acronyms are listed alphabetically. Alternatives to these acronyms are listed immediately below each of these entries, if they exist. Related acronyms (variations or subsets of techniques terminology used within the technique area) are grouped together below the major acronym and indented to the right. Most, but not all, of the techniques listed here are the subject of individual articles in this volume.

<p>AAS Atomic Absorption Spectroscopy</p> <p>AA Atomic Absorption</p> <p>VPD-AAS Vapor Phase Decomposition-Atomic Absorption Spectroscopy</p> <p>GFAA Graphite Furnace Atomic Absorption</p> <p>FAA Flame Atomic Absorption</p> <hr/> <p>AES Auger Electron Spectroscopy</p> <p>Auger Auger Electron Spectroscopy</p> <p>SAM Scanning Auger Microscopy</p> <p>SAM Scanning Auger Microprobe</p> <p>AED Auger Electron Diffraction</p> <p>ADAM Angular Distribution Auger Microscopy</p> <p>KE Kinetic Energy</p> <p>CMA Cylindrical Mirror Analyser</p> <p>AIS Assm Inelastic Scattering</p> <p>BET Brunauer, Emmett, and Teller equation</p> <p>BSDF Bidirectional Scattering Distribution Function</p> <p>BRDF Bidirectional Reflective Distribution Function</p> <p>BTDF Bidirectional Transmission Distribution Function</p> <hr/> <p>CL Cathodoluminescence</p> <p>CLSM Confocal Scanning Laser Microscope</p> <hr/> <p>EDS Energy Dispersive X-Ray Spectroscopy</p> <p>EDX Energy Dispersive X-Ray Spectroscopy</p> <p>EDAX Company selling EDX equipment</p> <hr/> <p>EELS Electron Energy Loss Spectroscopy</p> <p>HREELS High-Resolution Electron Energy-Loss Spectroscopy</p> <p>REELS Reflected Electron Energy-Loss Spectroscopy</p> <p>REELM Reflection Electron Energy-Loss Microscopy</p> <p>LEELS Low-Energy Electron Energy-Loss Spectroscopy</p>	<p>PEELS Parallel (Detection) Electron Energy-Loss Spectroscopy</p> <p>EXLEELS Extended Energy-Loss Fine Structure</p> <p>EELS Electron Energy-Loss Fine Structure</p> <p>CEELS Core Electron Energy-Loss Spectroscopy</p> <p>VEELS Valence Electron Energy-Loss Spectroscopy</p> <hr/> <p>EPMA Electron Probe Microanalysis</p> <p>Electron Probe Electron Probe Microanalysis</p> <hr/> <p>ERS Elastic Recoil Spectrometry</p> <p>HFS Hydrogen Forward Scattering</p> <p>HRS Hydrogen Recoil Spectrometry</p> <p>FRS Forward Recoil Spectrometry</p> <p>ERDA Elastic Recoil Detection Analysis</p> <p>ERD Elastic Recoil Detection</p> <p>PRD Particle Recoil Detection</p> <hr/> <p>EXAFS Extended X-Ray Absorption Fine Structure</p> <p>SEXAFS Surface Extended X-Ray Absorption Fine Structure</p> <p>NEXAFS Near-Edge X-Ray Absorption Fine Structure</p> <p>XANES X-Ray Absorption Near-Edge Structure</p> <p>XAFS X-Ray Absorption Fine Structure</p> <hr/> <p>FMR Ferromagnetic Resonance</p> <p>FTIR See IR</p> <p>FT Raman See Raman</p> <p>HREELS See EELS</p> <p>HRTEM See TEM</p> <hr/> <p>GDMS Glow Discharge Mass Spectrometry</p> <p>GDQMS Glow Discharge Mass Spectrometry using a Quadrupole Mass Analyser</p> <p>Glopiad Manufacturer name</p> <p>ICP-MS Inductively Coupled Plasma Mass Spectrometry</p> <p>ICP Inductively Coupled Plasma</p> <p>LA-ICP-MS Laser Ablation ICP-MS</p> <p>ICP-Optical Inductively Coupled Plasma Optical Emission</p> <p>ICP Inductively Coupled Plasma</p> <p>IETS Inelastic Electron Tunneling Spectroscopy</p> <p>IR Infrared (Spectrometry)</p> <p>FTIR Fourier Transform Infrared (Spectrometry)</p> <p>GC-FTIR Gas Chromatography FTIR</p> <p>TGA-FTIR Thermo Gravimetric Analysis FTIR</p> <p>ATR Attenuated Total Reflection</p>
--	---

46/120

23

Various analytical techniques (Cont.)



RA	Reflection Absorption (Spectroscopy)	SERS	Surface Enhanced Raman Spectroscopy
IRAS	Infrared Reflection Absorption Spectroscopy	RBS	Rutherford Backscattering Spectrometry
ISS	Ion Scattering Spectrometry	HEIS	High Energy Ion Scattering
LEIS	Low-Energy Ion Scattering	RHEED	Reflected High Energy Electron Diffraction
RCE	Resonance Charge Exchange	SREM	Scanning Reflection Electron Microscopy
LEED	Low-Energy Electron Diffraction	SALI	Surface Analysis by Laser Ionization
LIMS	Laser Ionization Mass Spectrometry	PSIMS	Pulsed Ionization Secondary Ion Mass Spectrometry
LAMMA	Laser Microprobe Mass Analysis	MNRPPI	Multi-Photon Nonresonant Post Ionization
LAMMS	Laser Microprobe Mass Spectrometry	MRRPPI	Multi-Photon Resonant Post Ionization
LIMA	Laser Ionization Mass Analysis	RPI	Resonant Post Ionization
NRMPI	Nonresonant Multi-Photon Ionization	MPI	Multi-Photon Ionization
MEISS	Medium-Energy Ion Scattering Spectrometry	SPF	Single-Photon Ionization
MEIS	Medium-Energy Ion Scattering	SIRIS	Spitzer-Initiated Resonance Ionization Spectroscopy
MOKE	Magneto-Optic Kerr Rotation	SARIS	Surface Analysis by Resonant Ionization Spectroscopy
SMOKE	Surface Magneto-Optic Kerr Rotation	TOFMS	Time-of-Flight Mass Spectrometer
NAA	Neutron Activation Analysis	SAM	See AES
INAA	Instrumental Neutron Activation Analysis	SEM	Scanning Electron Microscopy
NEXAFS	Near Edge X-Ray Absorption Fine Structure	SEM	Scanning Electron Microscopy
XANES	X-Ray Absorption Near Edge Structure	SE	Secondary Electron Microscopy
NIS	Neutron Inelastic Scattering	BSE	Secondary Electron Backscattered Electron
NMR	Nuclear Magnetic Resonance	SEMPA	Secondary Electron Microscopy with Polarization Analysis
MAS	Magic-Angle Spinning	SFM	Scanning Force Microscopy
NRA	Nuclear Reaction Analysis	AFM	Atomic Force Microscopy
OES	Optical Emission Spectroscopy	SFM	Scanning Probe Microscopy
PAS	Photoacoustic Spectroscopy	SIMS	Secondary Ion Mass Spectrometry
PIXE	Particle Induced X-Ray Emission	Dynamic SIMS	Dynamic Secondary Ion Mass Spectrometry
HIXE	Hydrogen/Helium Induced X-ray Emission	Static SIMS	Static Secondary Ion Mass Spectrometry
PL	Photoluminescence	Q-SIMS	SIMS using a Quadrupole Mass Spectrometer
PR	Photoresistance	Magnetic SIMS	Magnetic SIMS
EIBER	Electron Beam Electroresistance	Sector SIMS	See Magnetic SIMS
RDS	Reflection Diffraction Spectroscopy	TOF-SIMS	SIMS using Time-of-Flight Mass Spectrometer
Raman	Raman Spectroscopy	PISIMS	Post Ionization SIMS
FT Raman	Fourier Transform Raman Spectroscopy	SNMS	Sputtered Neutral Mass Spectrometry
RS	Raman Scattering	SNMSd	Secondary Neutral Mass Spectrometry
RRS	Resonant Raman Scattering	SNMSd	Direct Bombardment Electron Gas SNMS
CARS	Coherent Anti-Stokes Raman Scattering	SSMS	Spark Source Mass Spectrometry
		Spark Source	Spark Source Mass Spectrometry
		STEM	See TEM
		STM	Scanning Tunneling Microscopy

47/120

Various analytical techniques (Cont.)



SPM	Scanning Tunneling Microscope
SPM	Scanning Probe Microscopy
TEAS	Thermal Energy Atom Scattering
TEM	Transmission Electron Microscopy
CTEM	Conventional Transmission Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
HRTEM	High Resolution Transmission Electron Microscopy
SAD	Selected Area Diffraction
AEM	Analytical Electron Microscopy
CBED	Convergent Beam Electron Diffraction
LTEM	Lorentz Transmission Electron Microscopy
TLC	Thin Layer Chromatography
TSRLM	Tandem Scanning Reflected-Light Microscope
TSM	Tandem Scanning Reflected-Light Microscope
TXRF	See XRF
UPS	Ultraviolet Photoelectron Spectroscopy
MPS	Molecular Photoelectron Spectroscopy
VASE	Variable Angle Spectroscopic Ellipsometry
WDS	Wavelength Dispersive (X-Ray) Spectroscopy
WDX	Wavelength Dispersive X-Ray Spectroscopy
XAS	X-Ray Absorption Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy
ESCA	X-Ray Photoelectron Spectroscopy for Chemical Analysis
XPD	X-Ray Photoelectron Diffraction
PHD	Photoelectron Diffraction
KE	Kinetic Energy
XRD	X-Ray Diffraction
GIXD	Grazing Incidence X-Ray Diffraction
GIXRD	Grazing Incidence X-Ray Diffraction
DCD	Double Crystal Diffractometer
XRF	X-Ray Fluorescence
XFS	X-Ray Fluorescence Spectroscopy
TXRF	Total Reflection X-Ray Fluorescence
TXRF	Total Reflection X-Ray Fluorescence
VFD-TXRF	Vapor Phase Decomposition Total X-Ray Fluorescence

Encyclopedia of materials characterization
C. R. Brundell, C. A. Evans, Jr., S. Wilson,
Butterworth-Heinemann 1992

Total 183 techniques

Nanotechnology

Nano-characterization

48/120

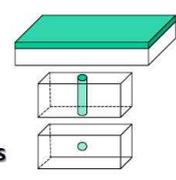
Nano-materials and analytic methods



1-dimensional : Quantum well, Thin films

2-dimensional : Quantum wire, Nanotubes

3-dimensional : Quantum dot, Nano-powders



Z \approx nm

X, Y \approx nm

X, Y, Z \approx nm

Method	Source	Sampling	Depth (Z)
XPS	X-ray	Photoelectron	1-10 nm
AES	<u>Electron</u>	<u>Auger electron</u>	2-6 nm
SIMS	Ion	Secondary ion	5-30 nm
RBS	He ion	Scattered ion	2-20 nm
SEM	<u>Electron</u>	<u>Secondary electron</u>	10 nm
EPMA	<u>Electron</u>	X-ray	1 μ m
TEM	<u>Electron</u>	<u>Transmitted Electron</u>	10 nm

49/120

Objectives of Analytical Methods



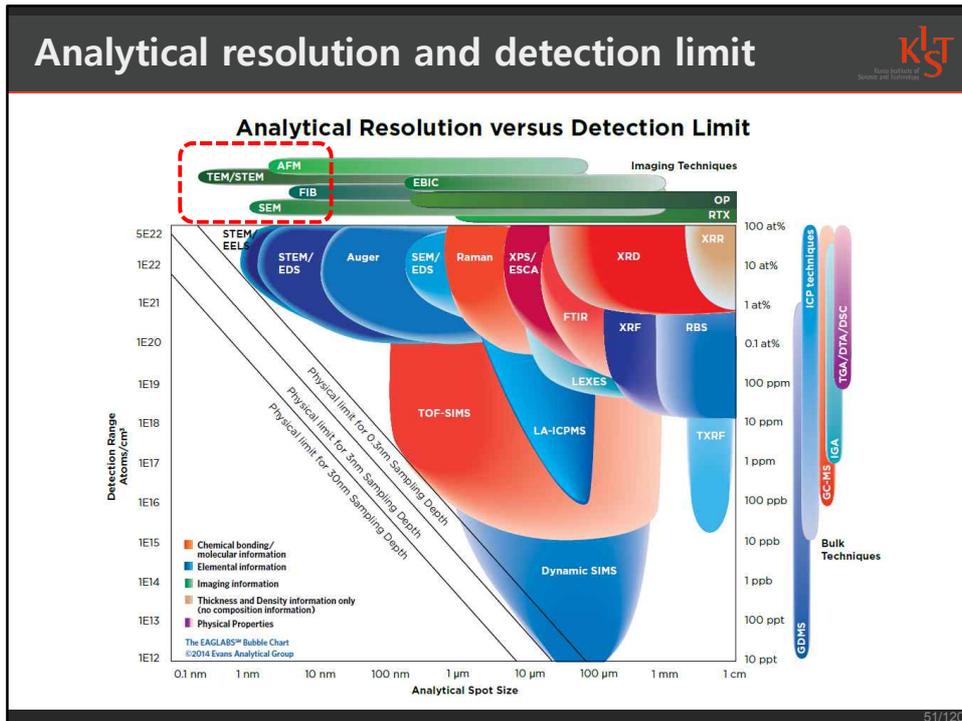
- **Identification** : Elements or compounds with high **sensitivity**
- **Quantification** : Concentration of elements with high **accuracy**
- **Localization** : Identification and quantification in the **small region**

➤ **Localization becomes an important factor in nano-materials**

Classification of Analytic techniques

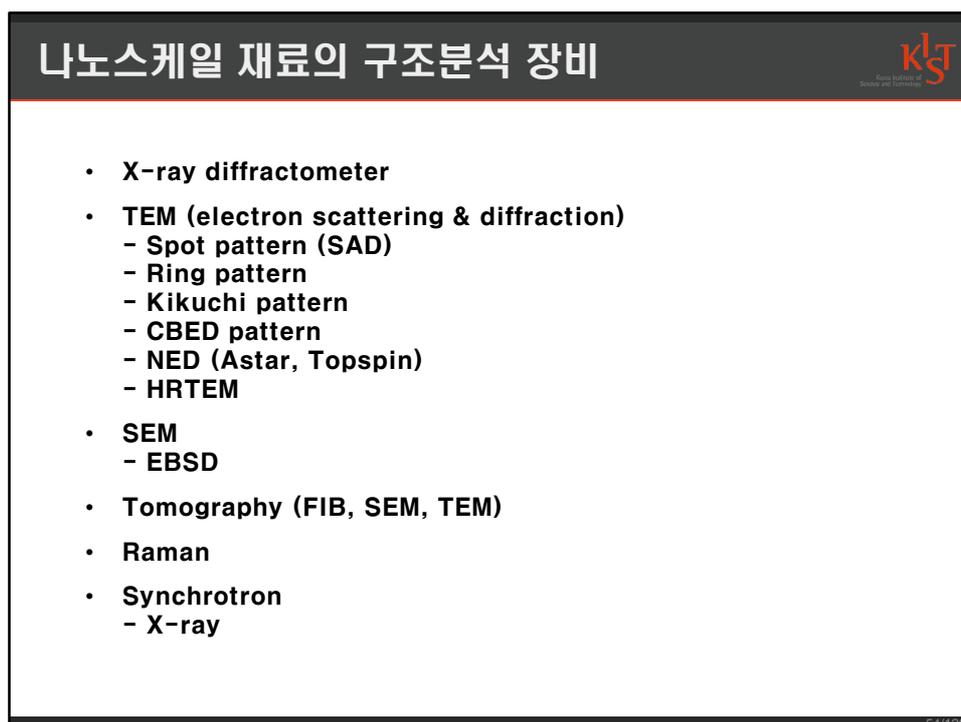
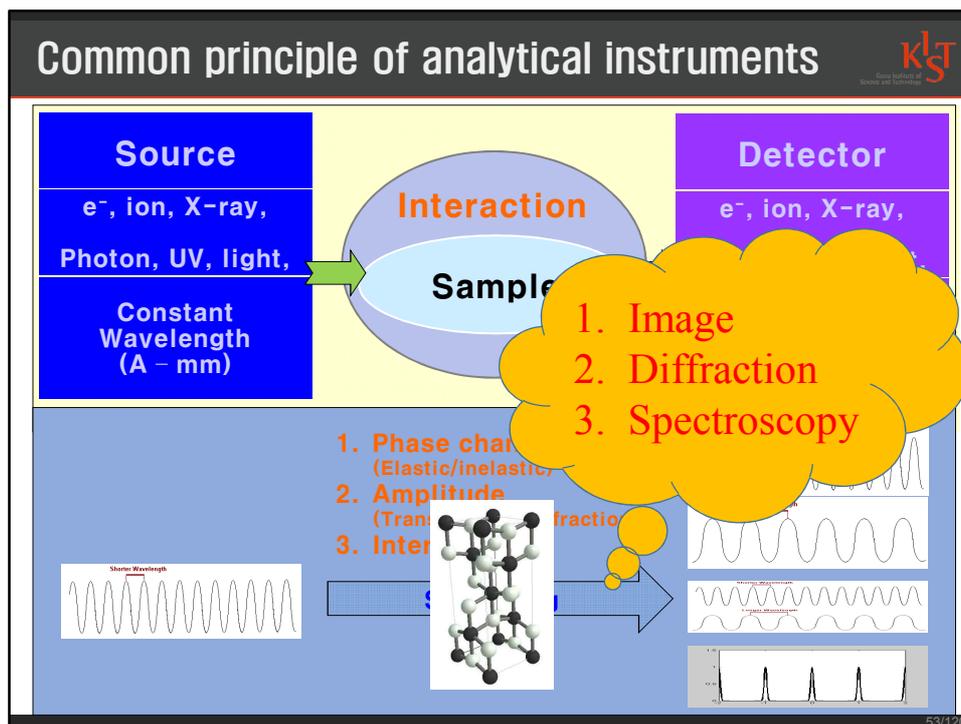
- **Nano-characterization** : **Region of analysis in nano-scale**
- **Surface analysis** : Information from the depth of about 5 nm
- **Thin film analysis** : Analysis for thin film and substrate (~ 1 μ m)
- **Bulk analysis** : Composition and microstructure in macro scale

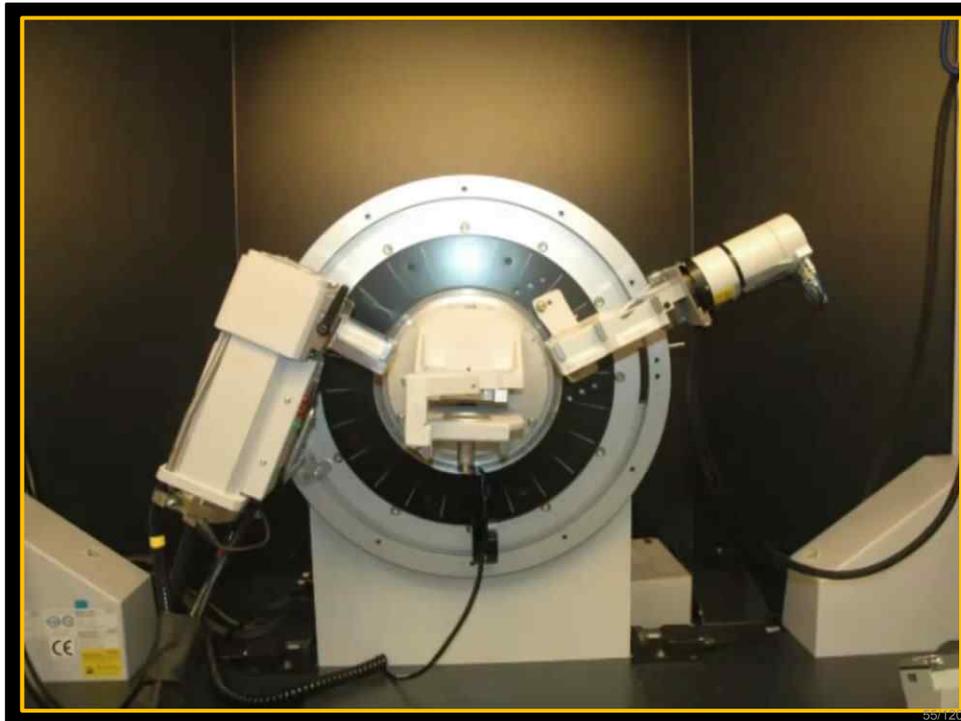
50/120



재료 분석장비의 간단한 원리

52/120



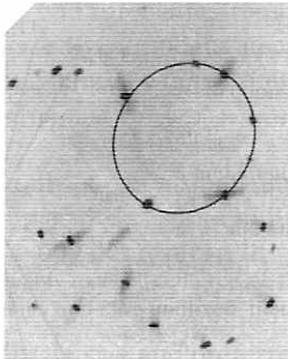
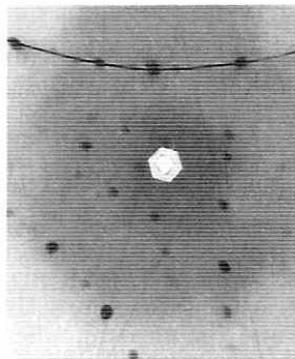


X-ray detector	
(1) 사진작용	사진 film
(2) 이온화작용	전리함(Ion Chamber) GM 계수관(Geiger-Muller Counter, GMC) 비례계수관(Proportional Counter, PC) 위치민감형 비례계수관(Position Sensitive Proportional Counter, 반도체 검출기(Solid-State Detector, SSD)
(3) 형광작용	형광판 Scintillation 계수관(Scintillation Counter, SC) X선(X-Rays) TV CCD Image Plate, IP
(4) 광전도작용	PbO(X선 TV)

Detector of X-ray



On film

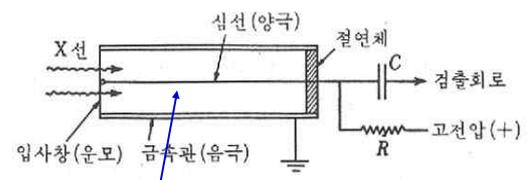
(a)
(b)

Fig 3-10. (a) Transmission and (b) back-reflection Laue patterns of an aluminum crystal (cubic). Tungsten radiation, 30KV, 19mA.

57/120



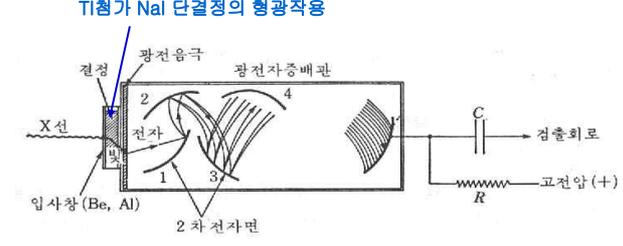
Proportional Counter



불활성가스(Ar, Kr, Xe 등) + (에테르, 알콜, Br₂, Cl₂)

Scintillation Counter

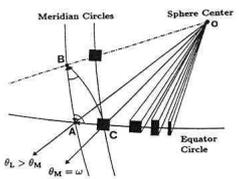
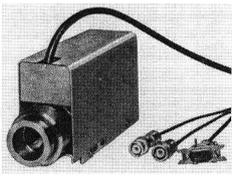
Tl첨가 NaI 단결정의 형광작용



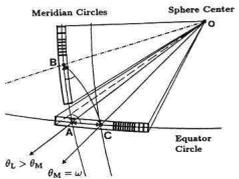
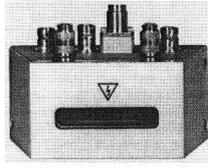
58/120

29

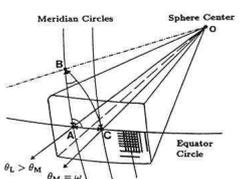
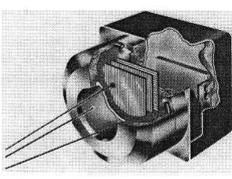
1. Zero-dimensional Point Detector (Single Detector)

2. One-dimensional Line Detector (Linear or curved PSD)

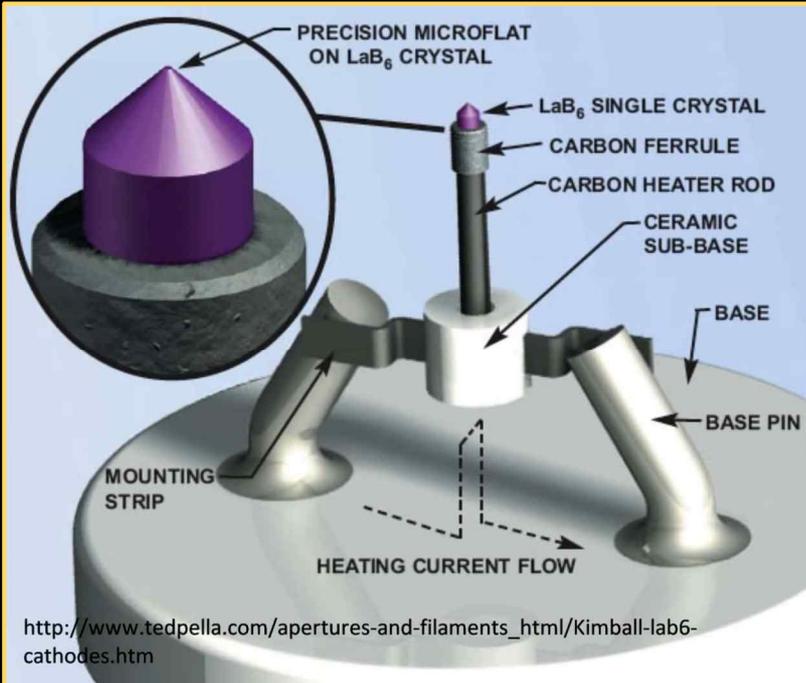



3. Two-dimensional Area Detector (Flat or concave PSD)

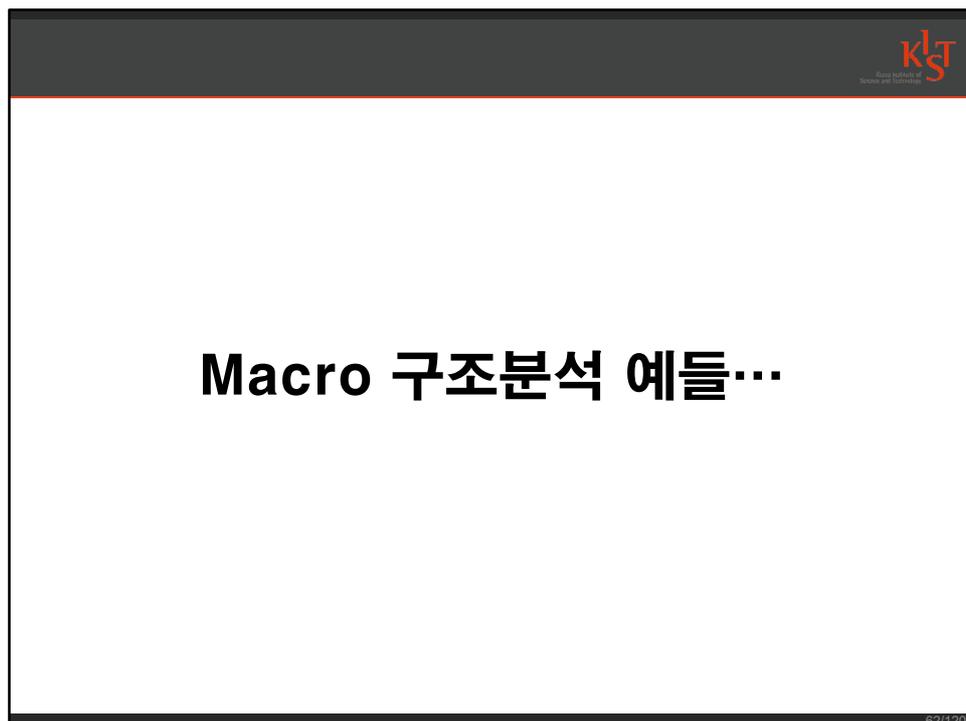
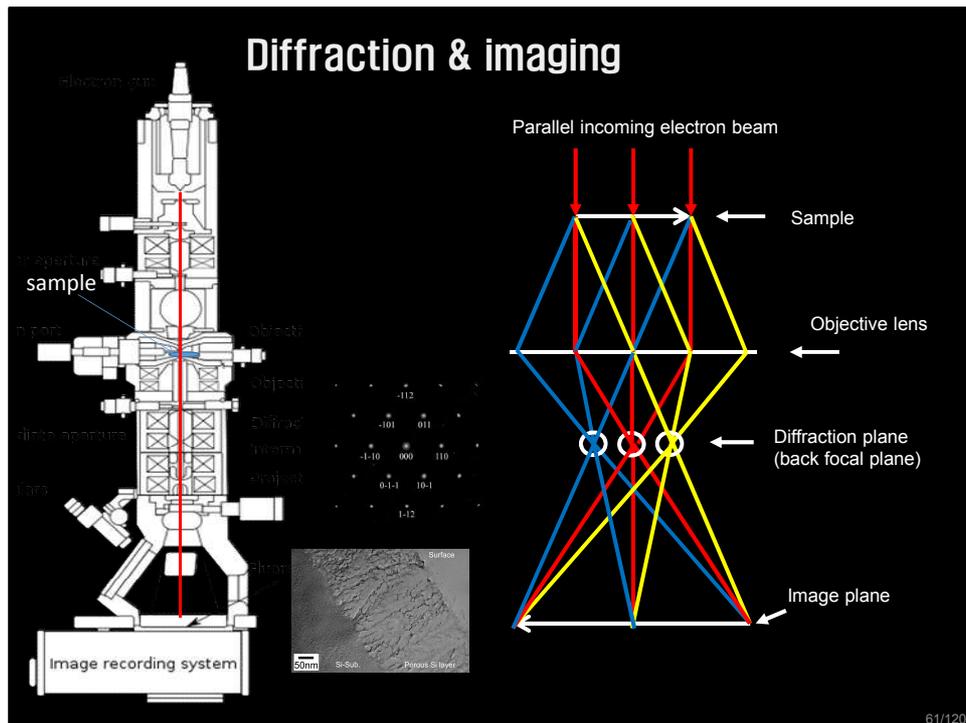


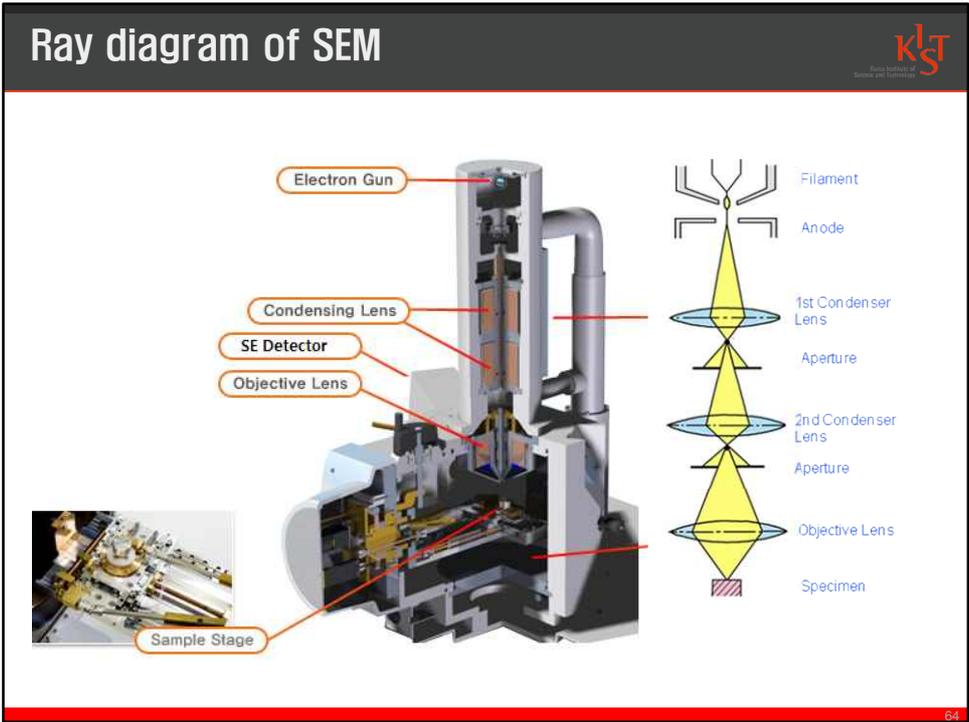
59/120

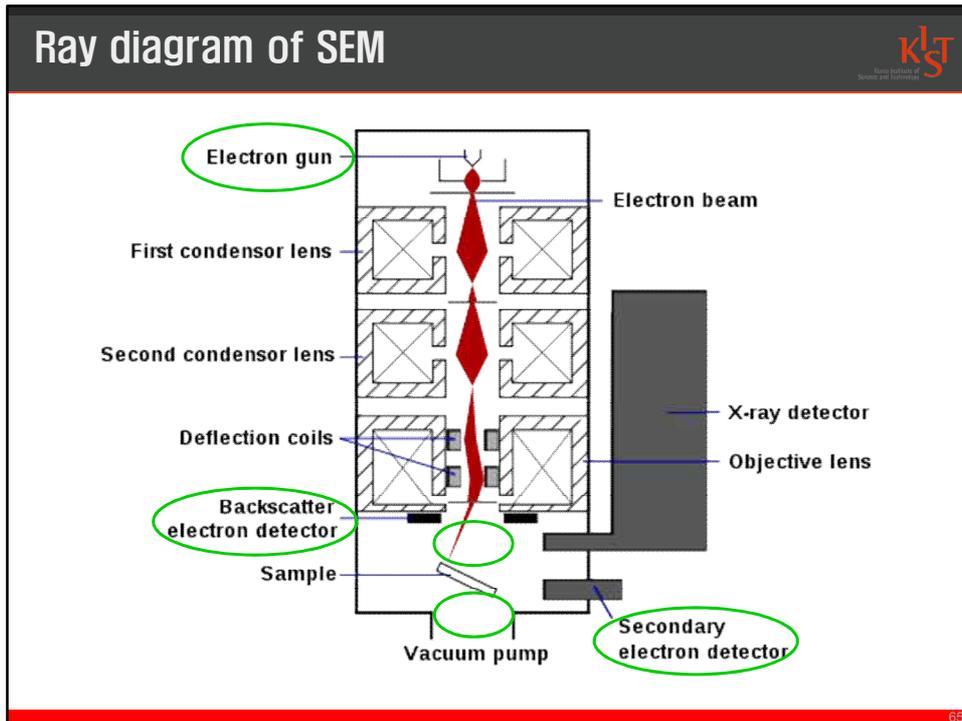


http://www.tedpella.com/apertures-and-filaments_html/Kimball-lab6-cathodes.htm

60/120







Scanning Electron Microscopes

Nano SEM

FE-SEM

E-SEM

EPMA

FEI XL-30 FEG ESEM

- ✓ 0.2 - 30 kV, 2 nm resolution
- ✓ 10 - 500,000x
- ✓ GSED, SE, BSE detector
- ✓ 10 - 10⁻⁸ torr
- ✓ Cathodoluminescence (180-850 nm)
- ✓ Heating stage (1500° C)
- ✓ Cooling stage (-30° C)
- ✓ Electron Backscatter Diffraction
- ✓ EDXS for chemical analysis

In-situ heating of WC-Co

Water condensation on Lotus leaf

Dualbeam Focused Ion Beam

FIB (Nova 600)

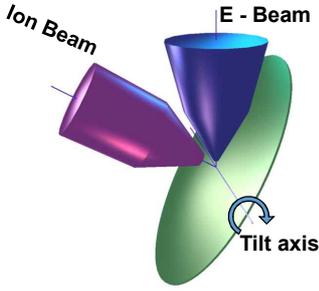
FIB (Helios)

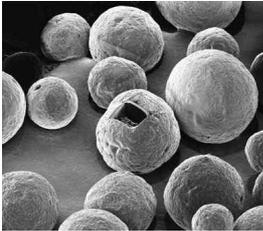
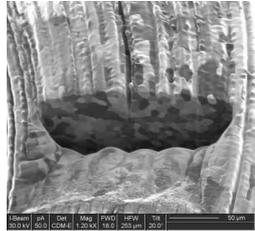
FIB (Quanta 3D)



FEI Nova NanoLab 600

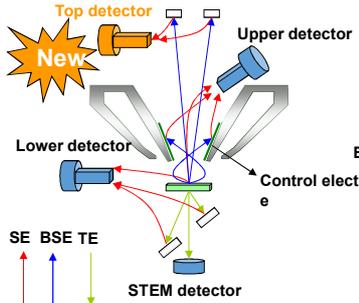
- ✓ FEG e-beam
- ✓ Ga⁺ ion beam
- ✓ Image resolution : 1 nm
- ✓ 5 - 30 kV, 250 - 1 Mx
- ✓ e-beam size : 0.3 nm and up
- ✓ Ion beam size : 5 - 500 nm
- ✓ Simultaneous milling / imaging



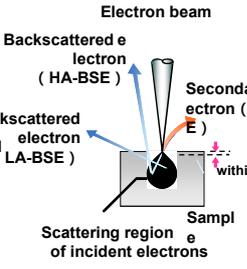



67/120

Top detector to obtain compositional/diffraction contrast of topmost surface



SE BSE TE
↑ ↑ ↓
STEM detector



Electron beam

Backscattered e⁻ electron (HA-BSE)

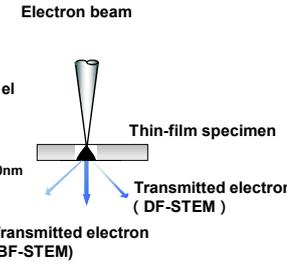
Backscattered electron (LA-BSE)

Secondary electron (SE)

Scattering region of incident electrons

Sample

within 10nm



Electron beam

Thin-film specimen

Transmitted electron (DF-STEM)

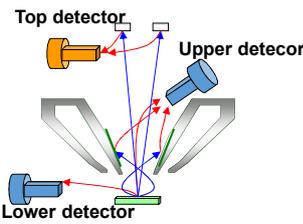
Transmitted electron (BF-STEM)

Signal	Abbrev.	Detector	Included information
Backscattered electron	HA-BSE	Top	Compositional + Crystal
Backscattered electron	LA-BSE	Upper	Compositional + Crystal +Topographical (with Charge reduction)
Secondary electron	SE	Upper	surface (incl. Voltage contrast)
Secondary electron	Lower	Lower	Topographical
Transmitted electron	BF-STEM	STEM	Internal + Crystal
Transmitted electron	DF-STEM	Lower	Internal + Compositional

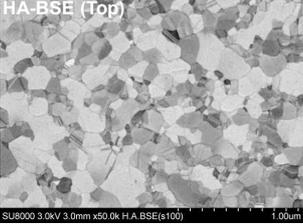
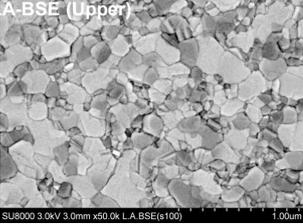
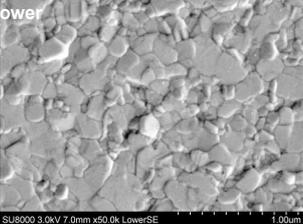
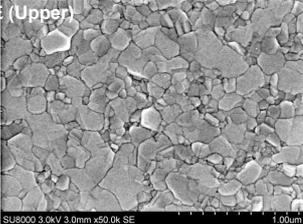
Enhanced signal detection performance



Different contrast from the same field of view for different purpose



Top detector
Upper detector
Lower detector

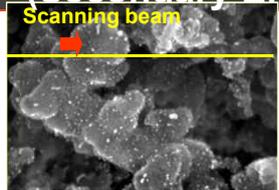





Signal (Detector)	Included information
HA-BSE (Top)	Compositional + Crystal
LA-BSE (Upper)	Compositional + Crystal + Topographical (with Charge reduction)
SE (Upper)	Topmost surface (Incl. Voltage contrast)
Lower SE (Lower)	Topographical

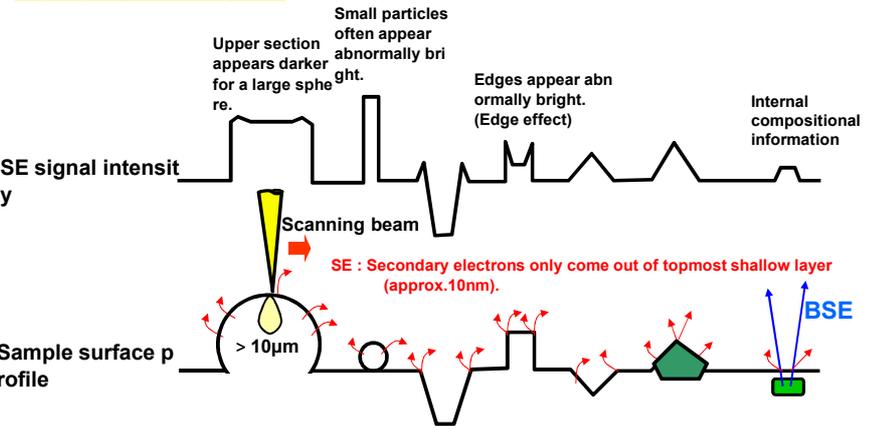
Sample : Surface of Au plating

Review of SEM basic (Secondary Electron excitation volume)





Scanning beam



Upper section appears darker for a large sphere.

Small particles often appear abnormally bright.

Edges appear abnormally bright. (Edge effect)

Internal compositional information

SE signal intensity

Scanning beam

SE : Secondary electrons only come out of topmost shallow layer (approx. 10nm).

Sample surface profile

> 10µm

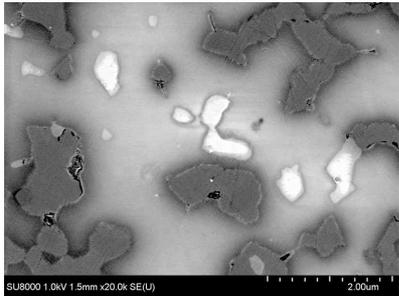
BSE

Charge reduction with LA-BSE

For engineers pursuing advanced technologies . . .

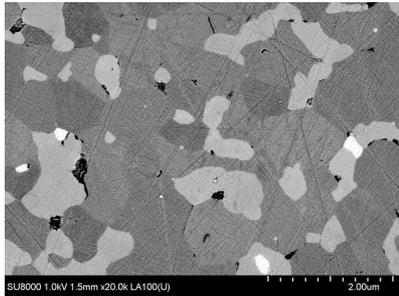
From high voltage imaging to low voltage imaging

Advantage
Reduction of local charging contrast using LA-BSE



SU8000 1.0kV 1.5mm x20.0k SE(U)
2.00um

Vacc :1kV
Imaging mode: **SE**



SU8000 1.0kV 1.5mm x20.0k LA100(U)
2.00um

Vacc : 1kV
Imaging mode : **LA-BSE**

Sample : AlTiC
(Nonconductive sample)

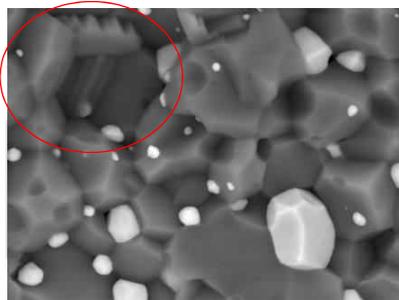
Low acceleration voltage BSE image

For engineers pursuing advanced technologies . . .

From high voltage imaging to low voltage imaging

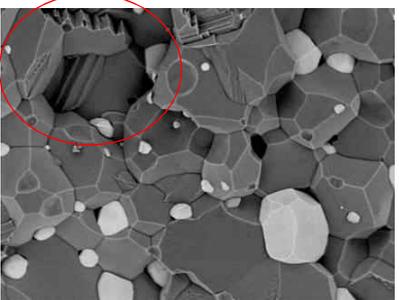
Advantage

- Small interaction volume contributes to the high resolution BSE image including surface information



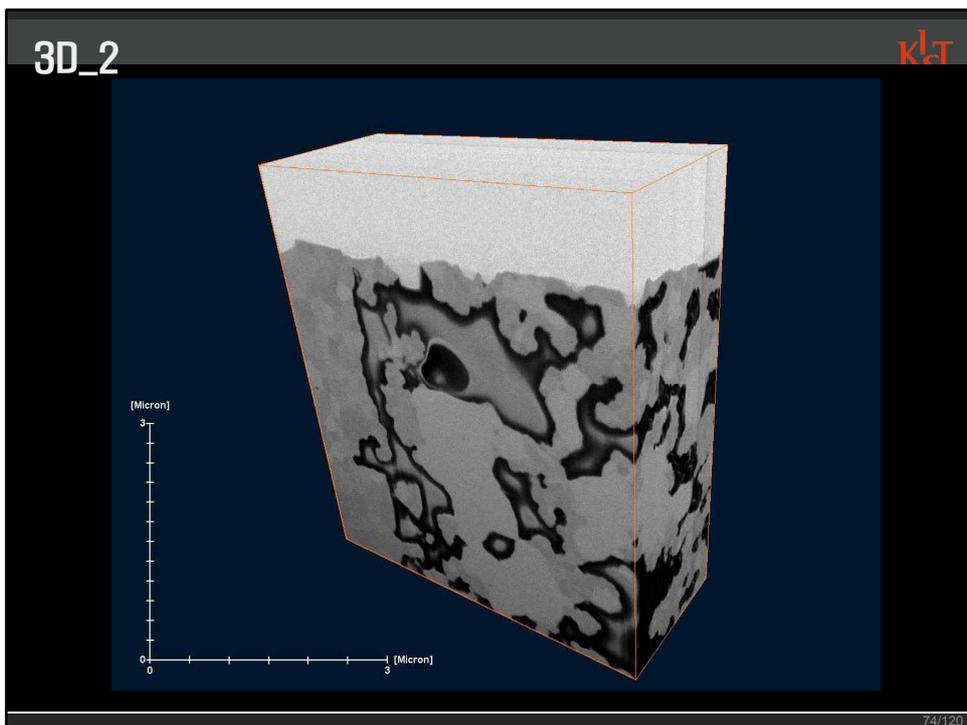
Monte Carlo simulation
incident Volume (Si)

Vacc :**10kV**
Imaging mode: **BSE**



Sample : Ni-Al alloy

Vacc : **1kV**
Imaging mode : **BSE**





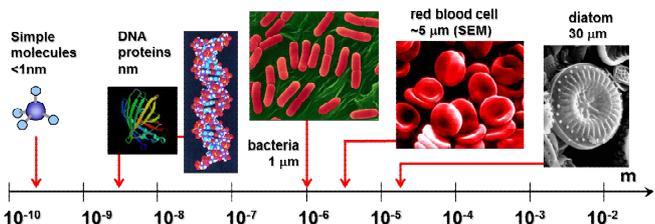
Nano 구조분석 예들...

75/120



Nano-characterization, Micron to Nano

- Identification and quantification in the nanometer region
 - Building blocks / electronic structures
 - Arrangement of building blocks
 - Mechanical response / chemical reaction etc.
- Chemical and Physical properties.
 - How the material "behaves" at the nano-scale!



Analytical TEM
 DualBeam FIB
 Analytical SEM

← Higher resolution Larger field of view →

76/120

Nano-characterization, Micron to Nano

Crystal structure
Nanostructure
Chemistry

Information \updownarrow

Morphology
Chemistry

Requirements

\triangleright Imaging resolution	nm	\leftrightarrow	Å
\triangleright Analytical resolution	μ m	\leftrightarrow	nm
\triangleright Sample size	150 mm	\leftrightarrow	10 μ m
\triangleright Sample preparation	Bulk	\leftrightarrow	Foil
\triangleright Contrast mechanism	Topography	\leftrightarrow	Diffraction
\triangleright Dimensions	Projection	\leftrightarrow	Tomography

77/120

Microscopes for Nano-Analysis

Analytical SEM

DualBeam FIB

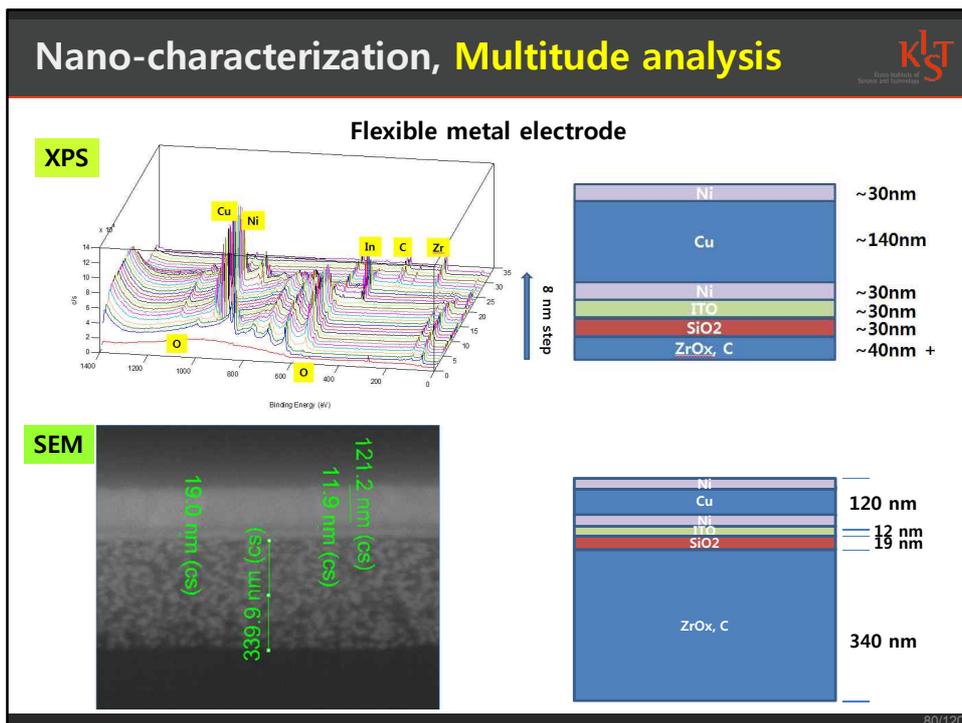
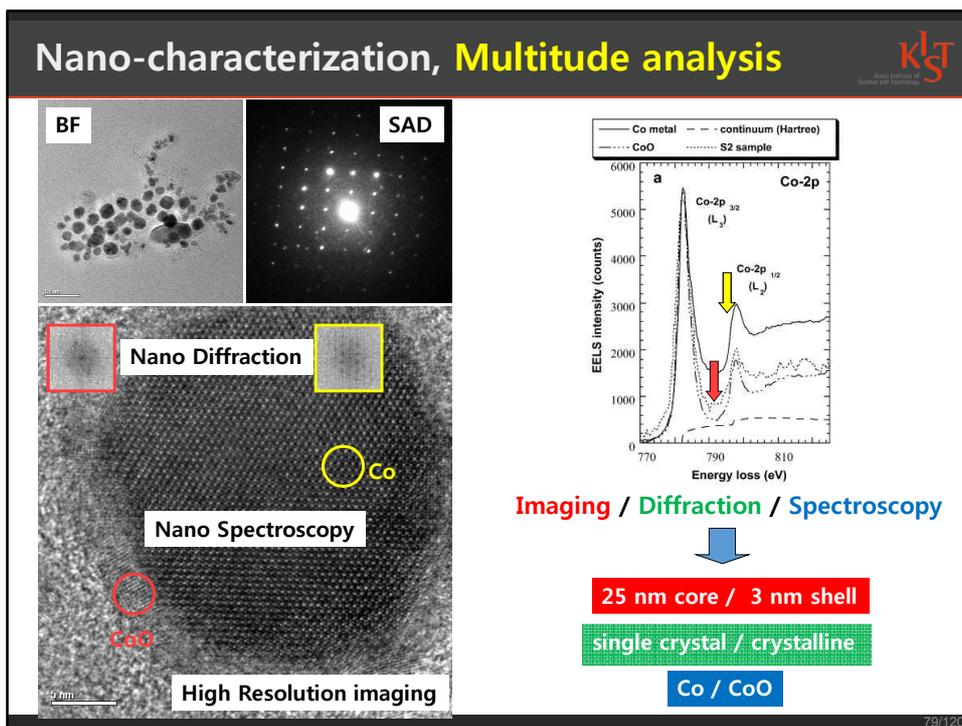
Analytical TEM

Large area surface imaging

Large area sub-surface imaging

Small area internal imaging

78/120



KIST
Korea Institute of Science and Technology

Nano-characterization, Multitude analysis

TEM

100 nm

10 nm

5.1 nm

Element	Weight %	Atomic %
O(K)	21.050	31.881
Si(K)	78.949	68.118

영상면 : 미세구조 관찰 (영상분해능 ~ 0.1 nm)
회절면 : 결정구조 분석 (공간분해능 ~ 0.1 nm)
EDS면 : 화학조성 분석 (공간분해능 ~ 0.1 nm)

18 nm Ni + Cu + Cr

98 nm Cu

12 nm Ni + Cu + Cr

19 nm ITO crystalline

7 nm SiO₂ amorphous

470 nm Monoclinic ZrO₂ + PET

81/120

KIST
Korea Institute of Science and Technology

In-situ TEM (gas, liquid, T, P)

82/120

In-situ 실험, 이젠 leading trend !

Kinetics

Cooling & heating

스펙트럼

EDX

광학

CL

전기적 특성 측정과 구조분석을 동시에 수행하여
하나의 시료로부터 종합적인 정보를 추출함

기계적특성

Nano probe

구조분석

FIB **TEM**

전기적특성

소자제작 **전기특성** **I-V**

83 / 93 83 / 120

In-situ 실험, 이젠 leading trend !

$MgH_2 \rightleftharpoons Mg$

분말

20 μm

단면노출

TEM

100 nm

(a)

100 nm

- 국부적인 반응에 대한 측정과 관찰을 동시에 수행함
- 의미 있는 영역에서 TEM까지 관찰
- 조성분석

1)J.W. Kim, Scripta materialia, 62 9 2010, 2)S.A Jin, Acta materialia, 55 15 2007, 3)J.W. Kim, Scripta Materialia, 60 12 1089 2009
4)S.A. Jin, J. Power Sources, 179 1 373 2008, 5)J.W. Kim, Materials Letters 62 16 3461 2008

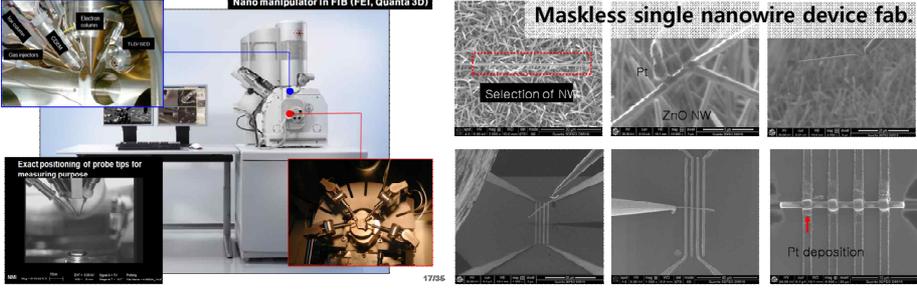
84 / 120

Nano-characterization, Property measurement

DualBeam FIB + **Nanomanipulator system**

Nano manipulator in FIB (FEI, Quanta 3D)

Maskless single nanowire device fab.



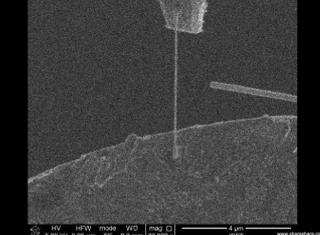
Selection of NW

Pt

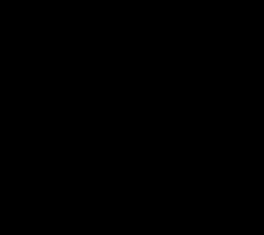
ZnO NW

Pt deposition

Mechanical testing of nanowire



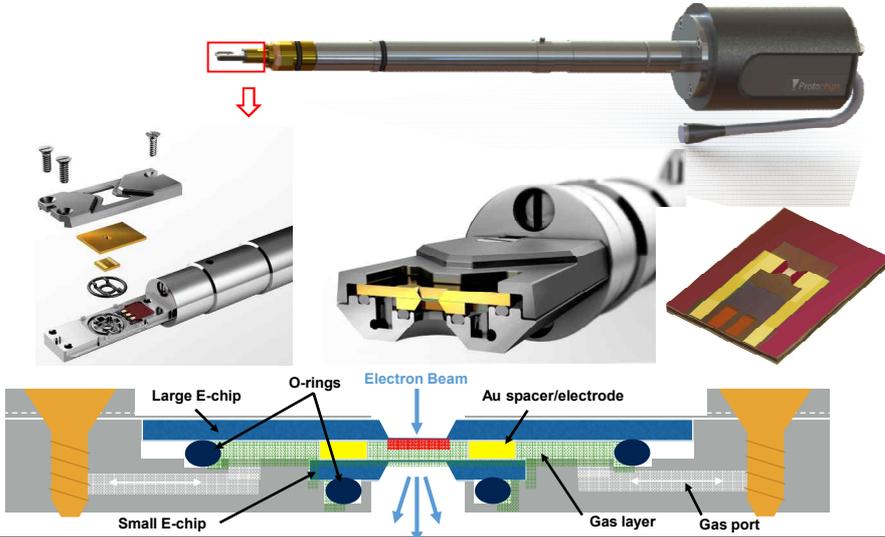
Super-Elastic behavior of nanowire



85/120

in-situ Gas holder demo 실시

» **Atmosphere (Protochips, Gas holder)**



Large E-chip

O-rings

Electron Beam

Au spacer/electrode

Small E-chip

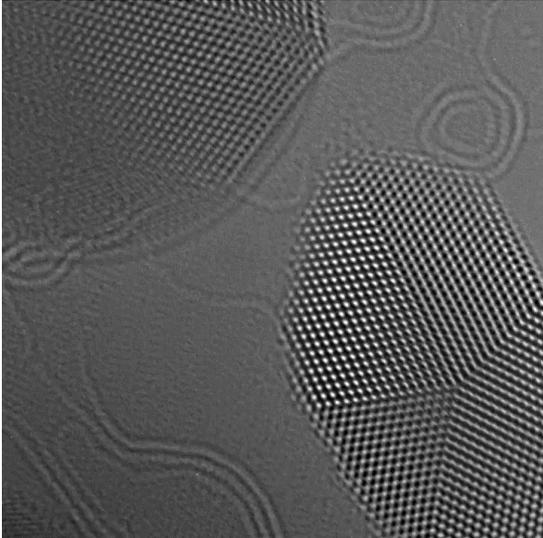
Gas layer

Gas port

86/120

In-situ heating





Surface change of Au nanoparticles at 600°C

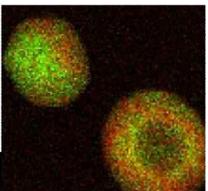
<https://www.youtube.com/watch?v=Itq2Qy-UKx0>, from Proto chips

87/120

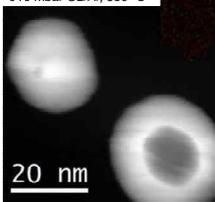
EDS & EELS analysis at specific pressure and temperature



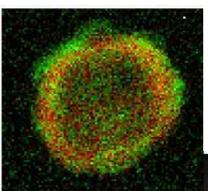
EDS SI, Pd/Ag



910 mbar O₂/Ar, 350 °C

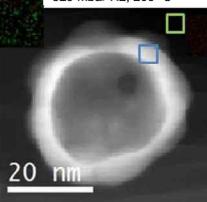


20 nm

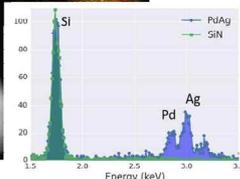
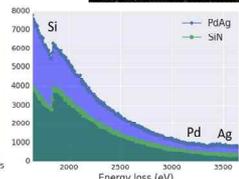


EELS SI, Pd/Ag

820 mbar H₂, 200 °C



20 nm

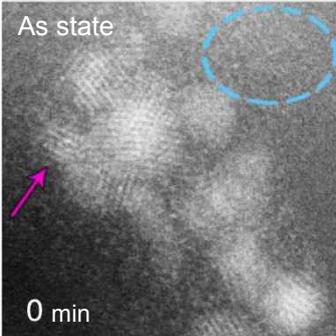
Pd/Ag Nanoparticles
 FEI Titan ChemiSTEM w/ SuperX EDS
 Image courtesy U Manchester

88/120

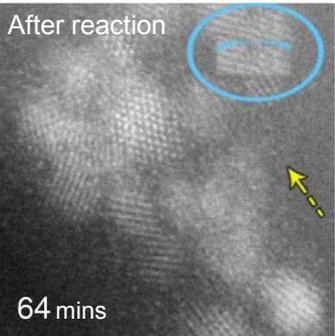
CASE-2 : Methane combustion catalysts



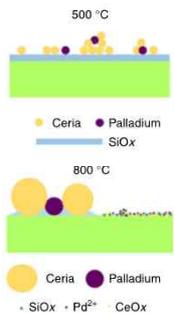
- **Solution:** Atmosphere system with 150 Torr O₂ to mimic calcination conditions
- **Results:** Confirmed the formation of the two distinct structures – larger nanoparticles and highly dispersed atomic-scale clusters possibly stabilized by silicon.



As state
0 min



After reaction
64 mins



500 °C
800 °C

● Ceria ● Palladium
— SiOx

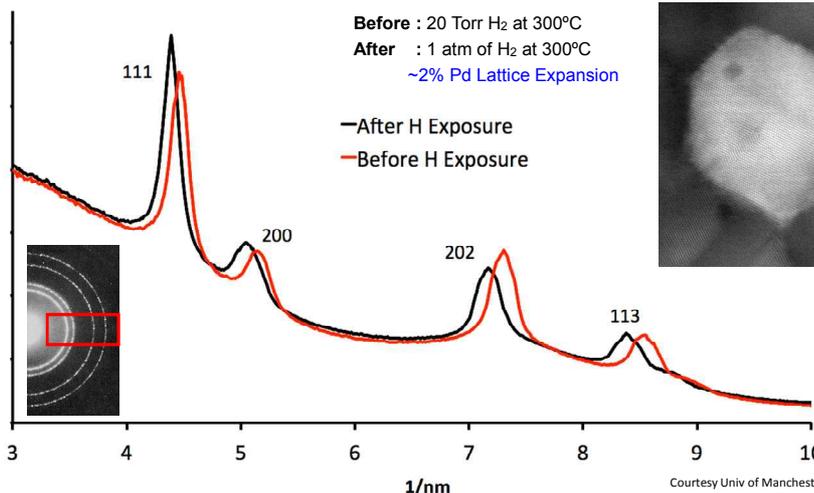
● Ceria ● Palladium
• SiOx • Pd²⁺ • CeOx

Pd@CeO₂ At 150 Torr O₂, 500 °C

Zhang, Shuyi, et al. Nature communications 6 (2015). 7778- 89/120

Case-3 : Hydrogen absorption in palladium

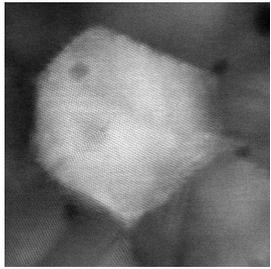


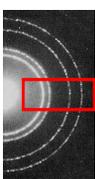


Before : 20 Torr H₂ at 300°C
After : 1 atm of H₂ at 300°C
~2% Pd Lattice Expansion

— After H Exposure
— Before H Exposure

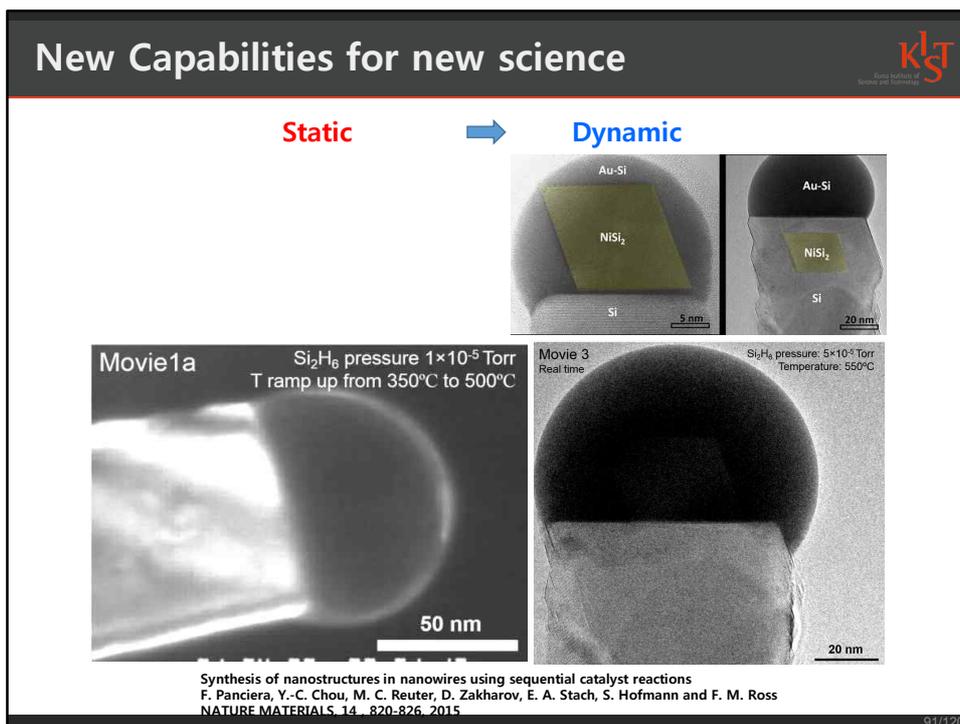
1/nm





Courtesy Univ of Manchester
& Karlsruhe Inst of Tech
FEI Titan

Protochips Application notes. AG80.3 90/120



제언

- 2017년 국가연구장비 현황
- SEM과 TEM의 주요 기능에 바탕을 둔 주변 장비
 - ion miller
 - cp
 - in-situ TEM (Protochips, Dens)
 - in-situ SEM
 - Air SEM
 - Plasma cleaner
 - SEM-groove box 연결
- 전자현미경의 진화를 위한 진공기술
(조인트, 플랜지, 펌프, 피드쓰루, 디텍터, 노이즈)

92/120



KIST
Korea Institute of Science and Technology

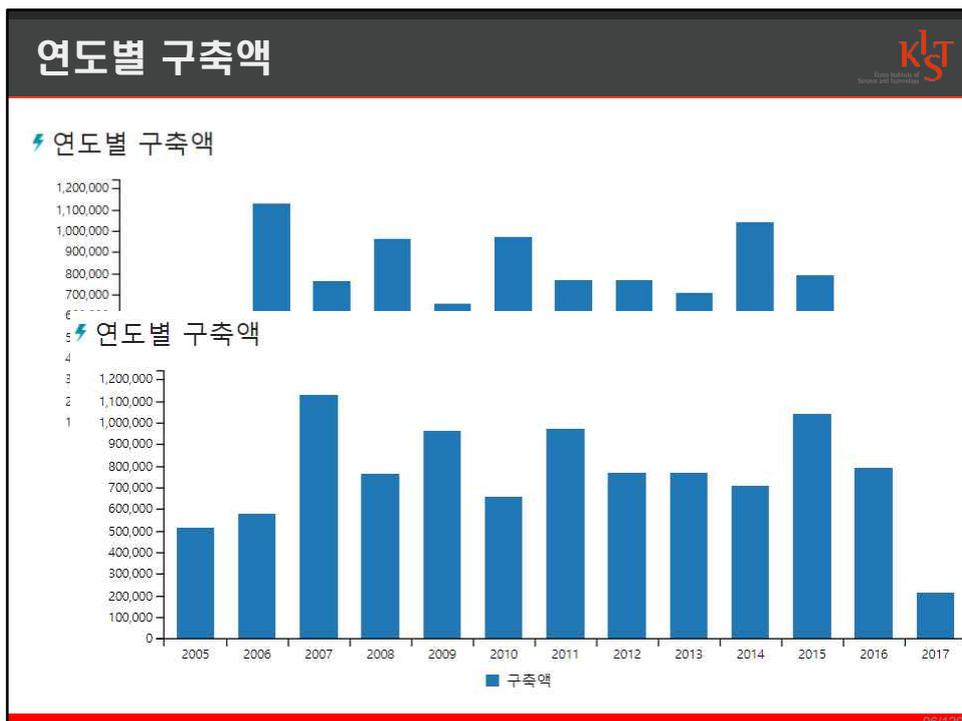
보조자료

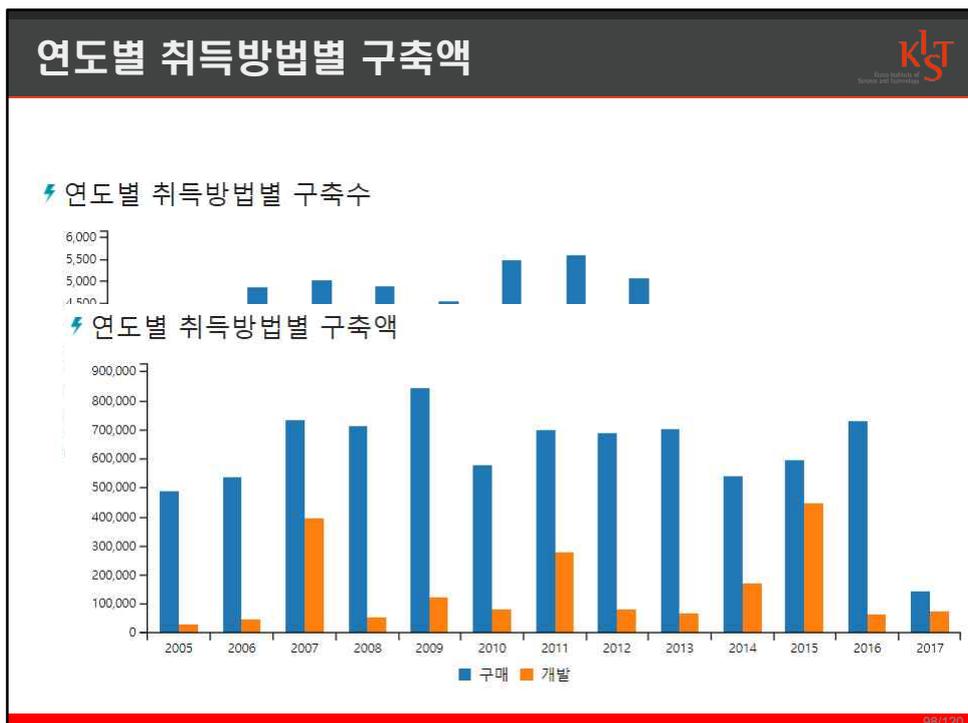
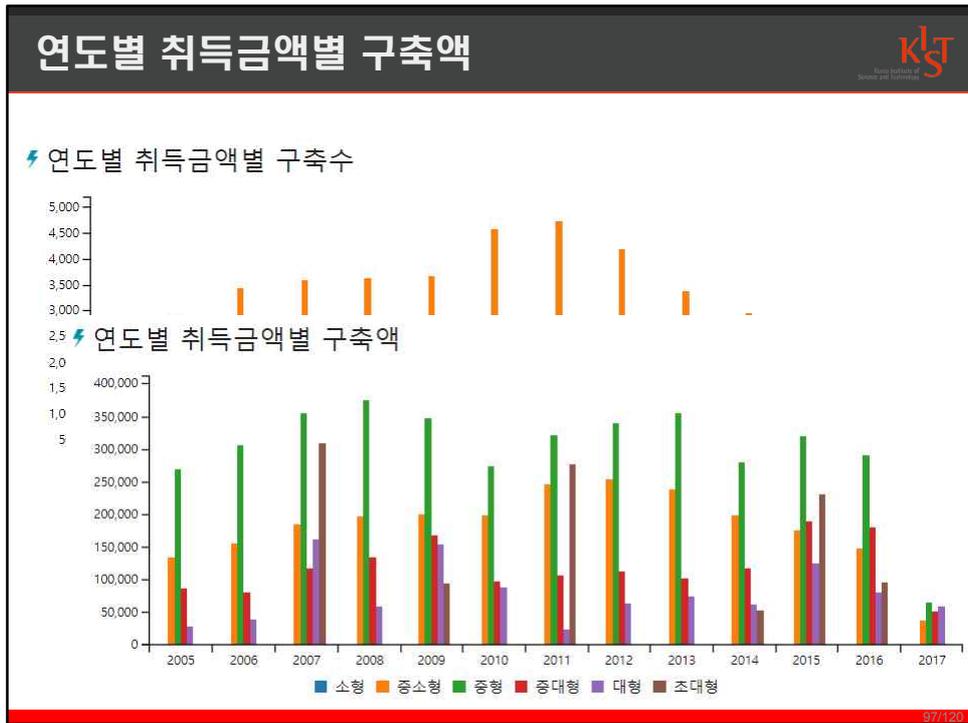
94/120

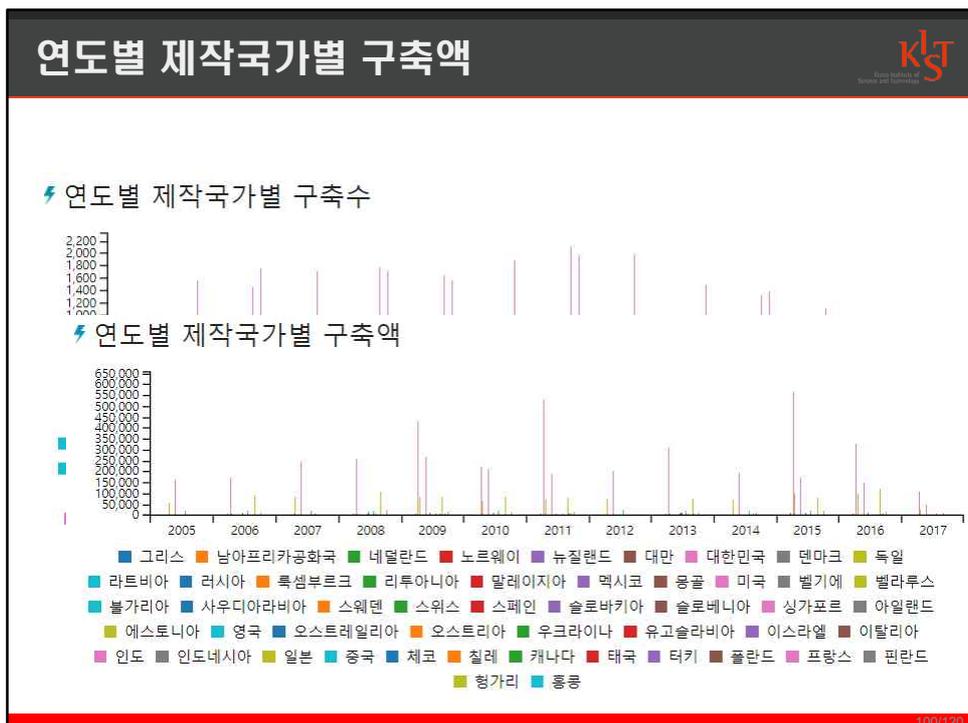
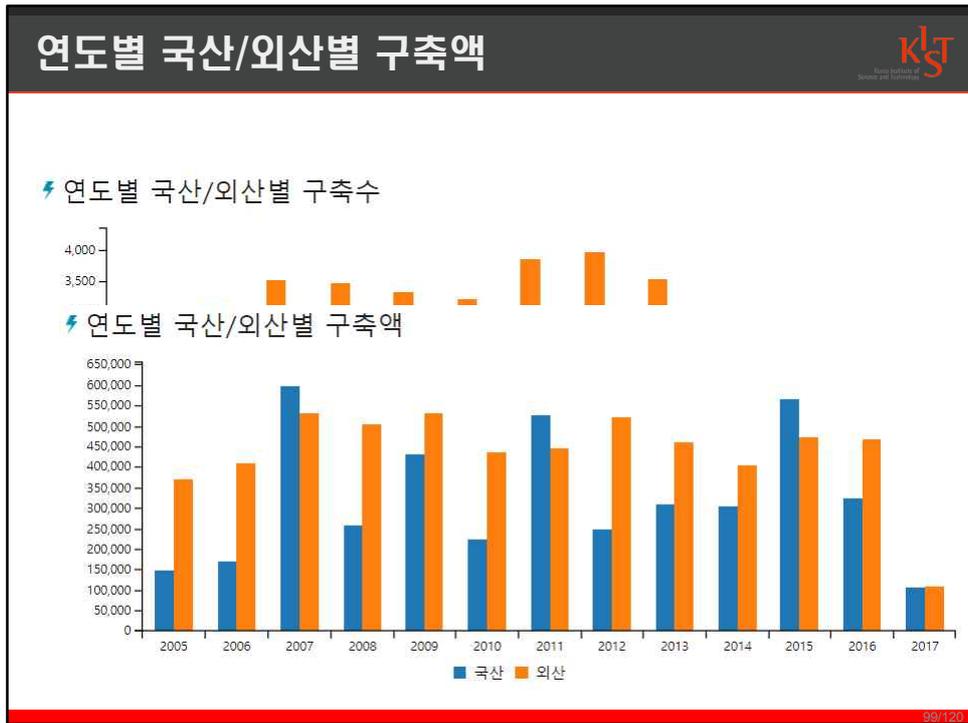

Korea Institute of Science and Technology

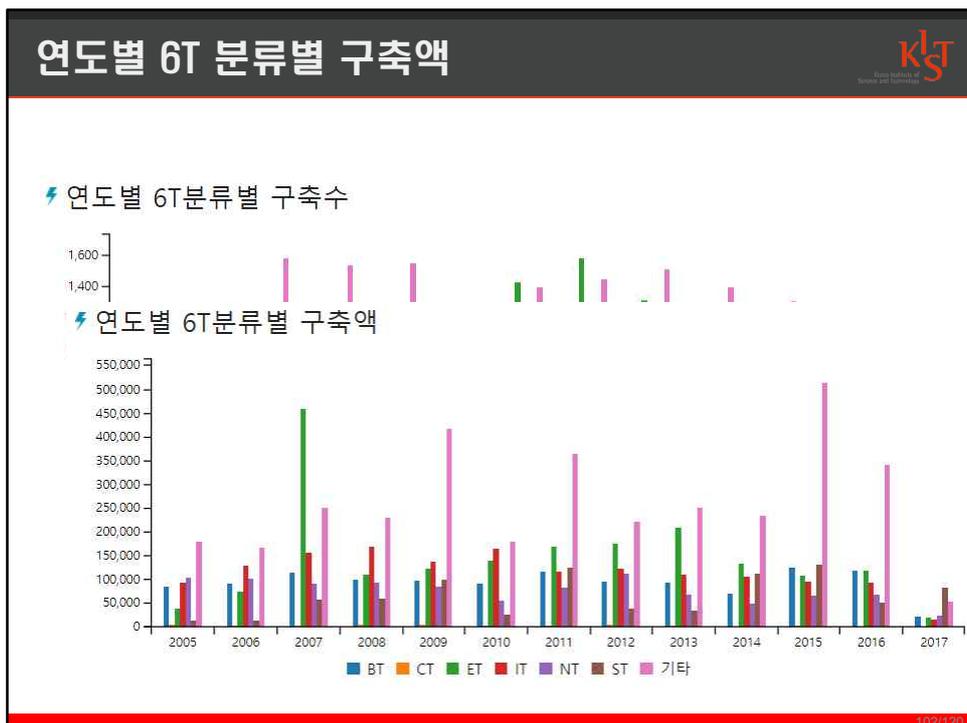
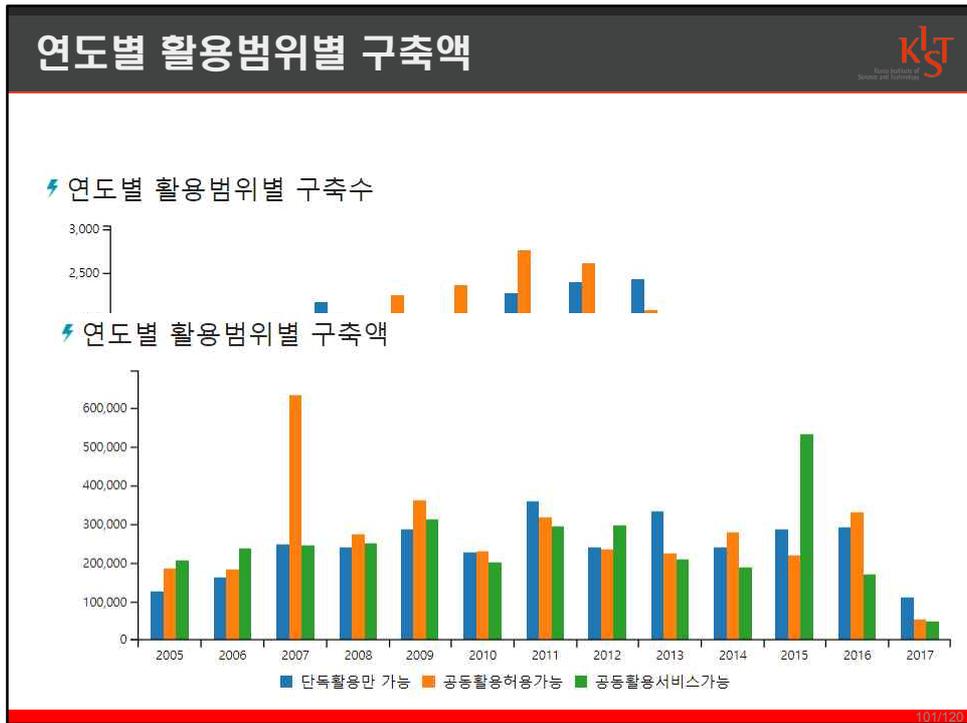
2017년 국가연구장비 현황

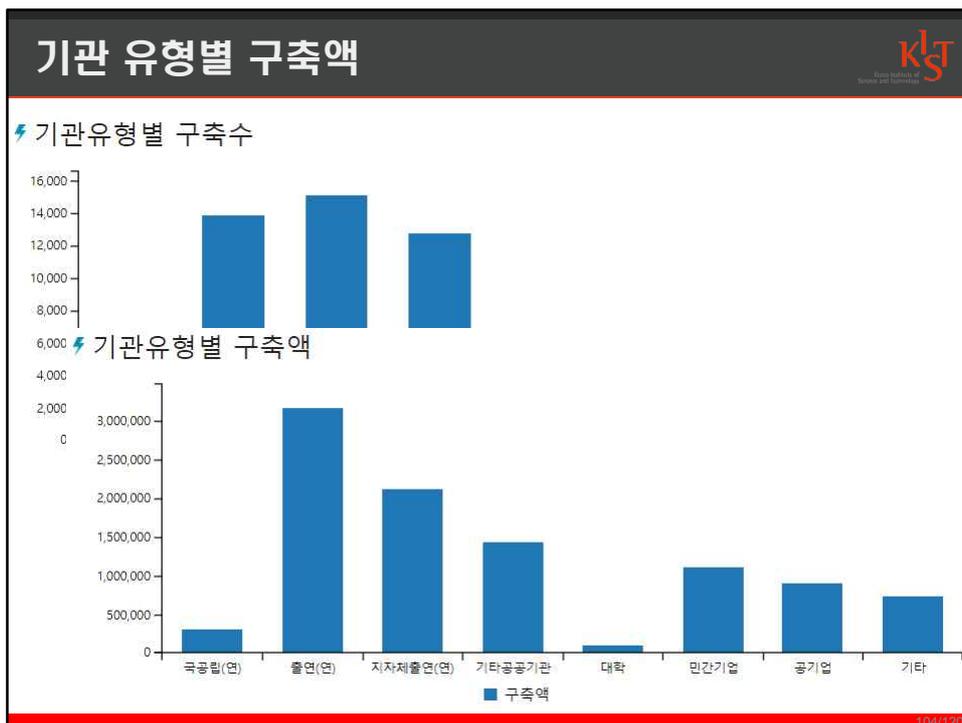
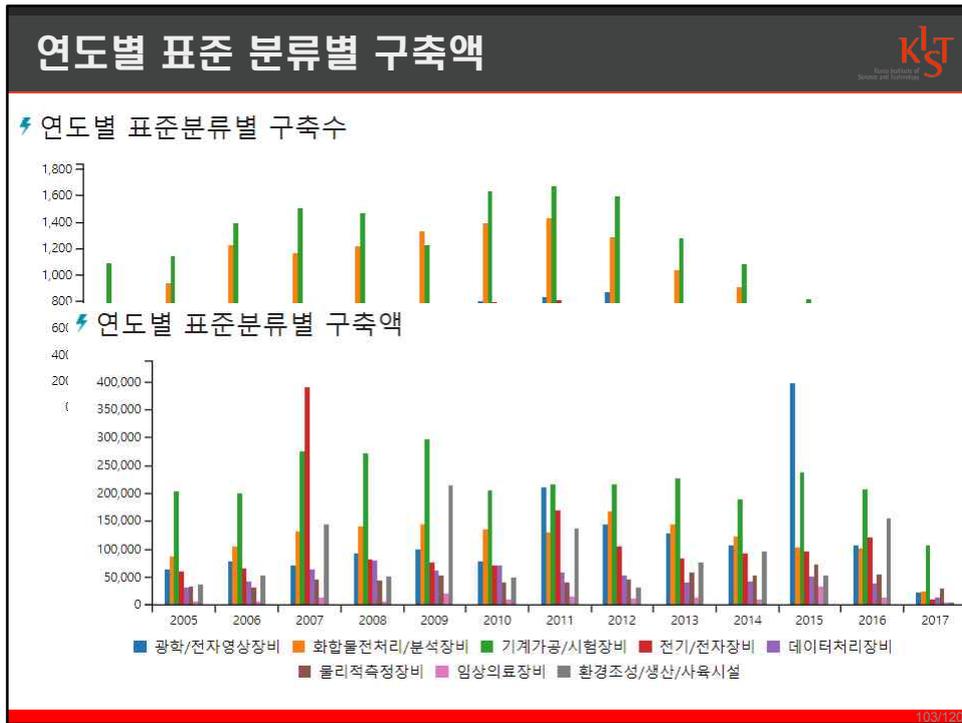
95/120

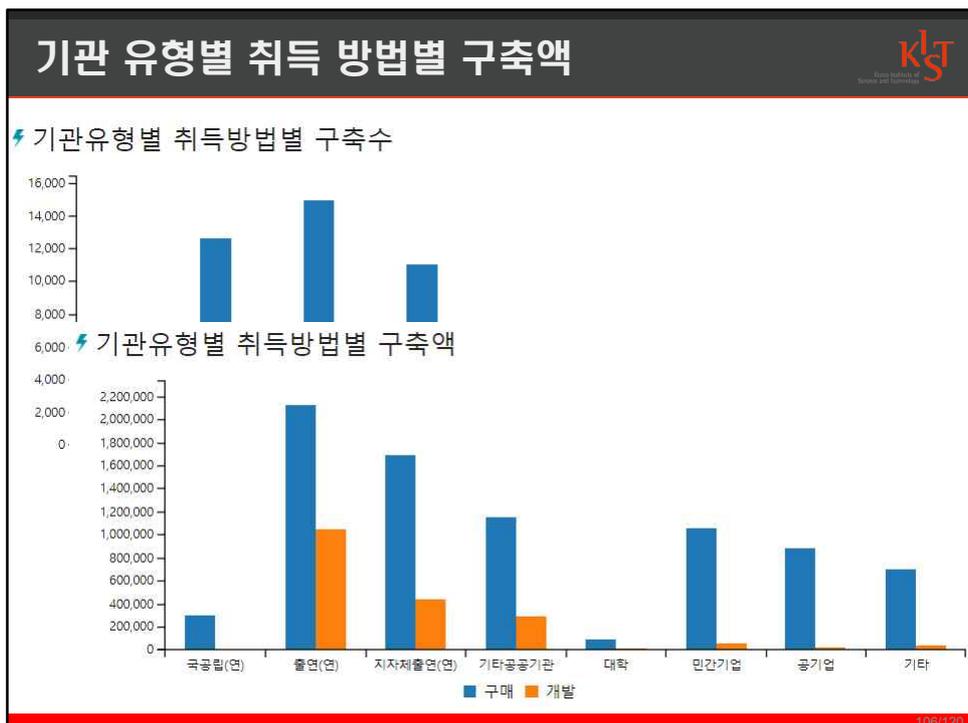
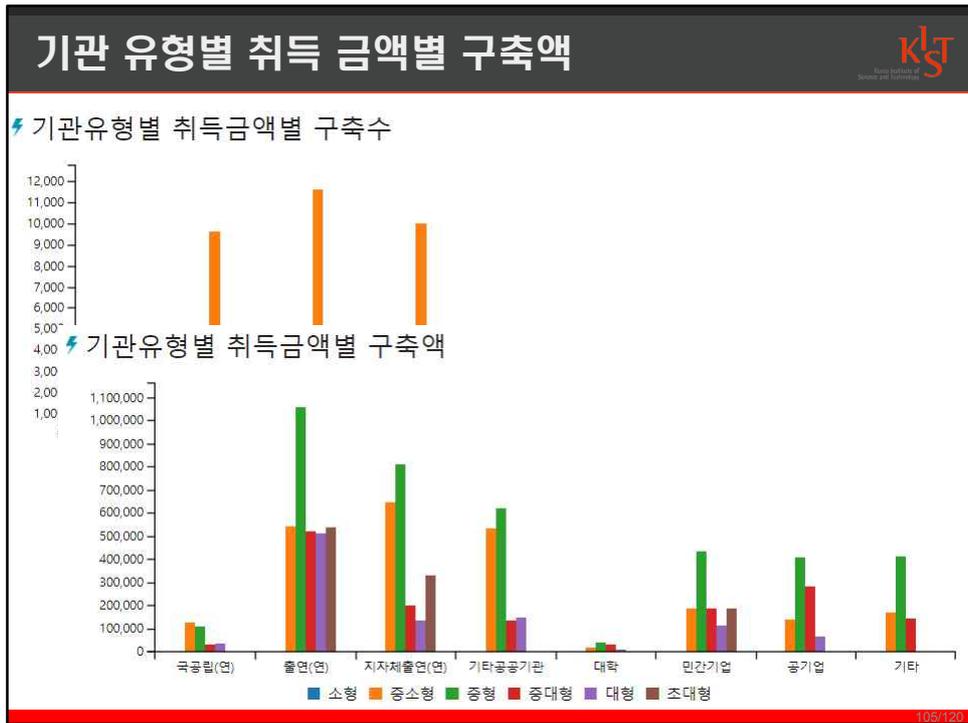


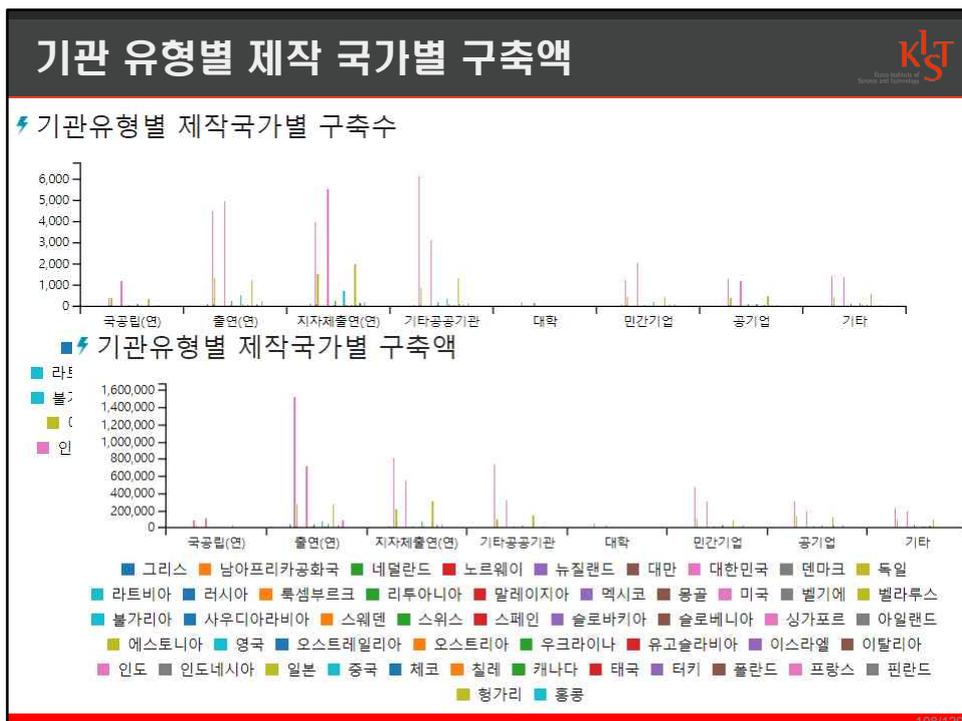
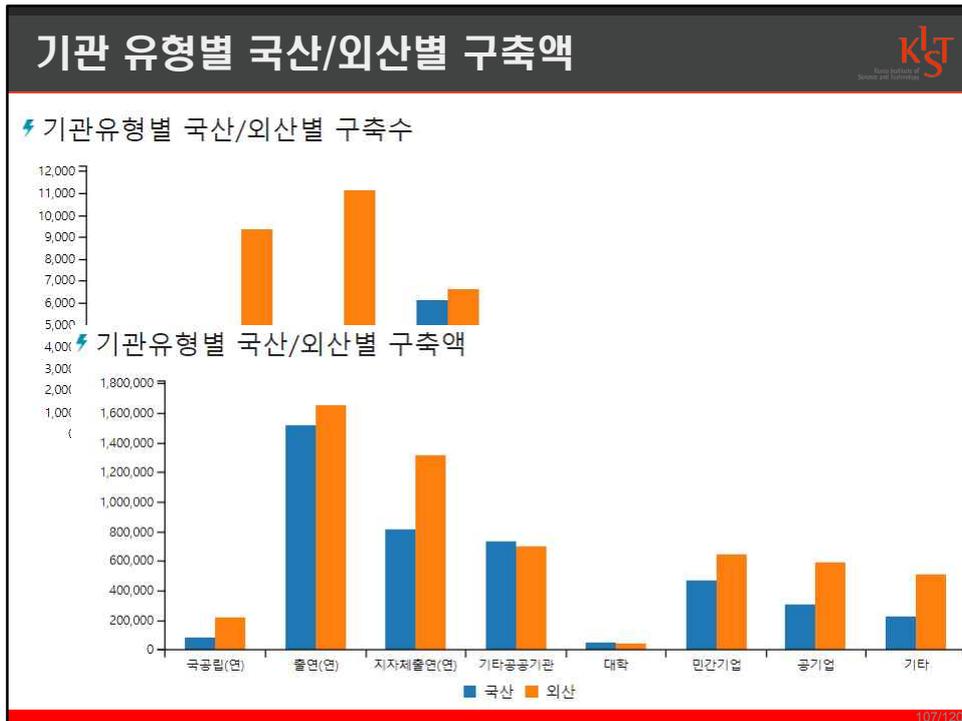


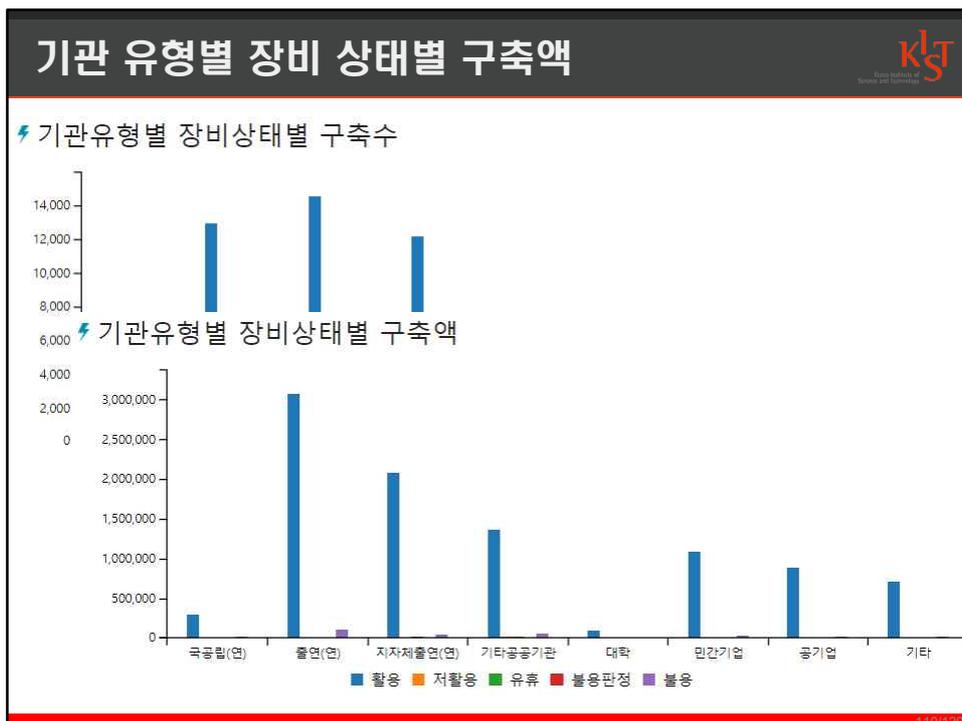
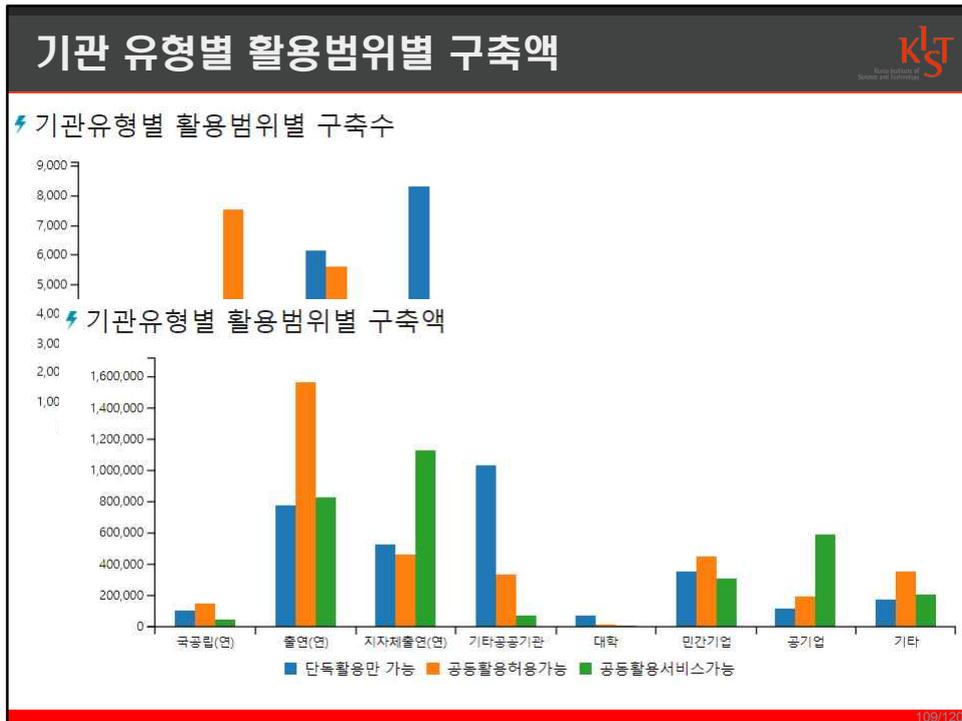


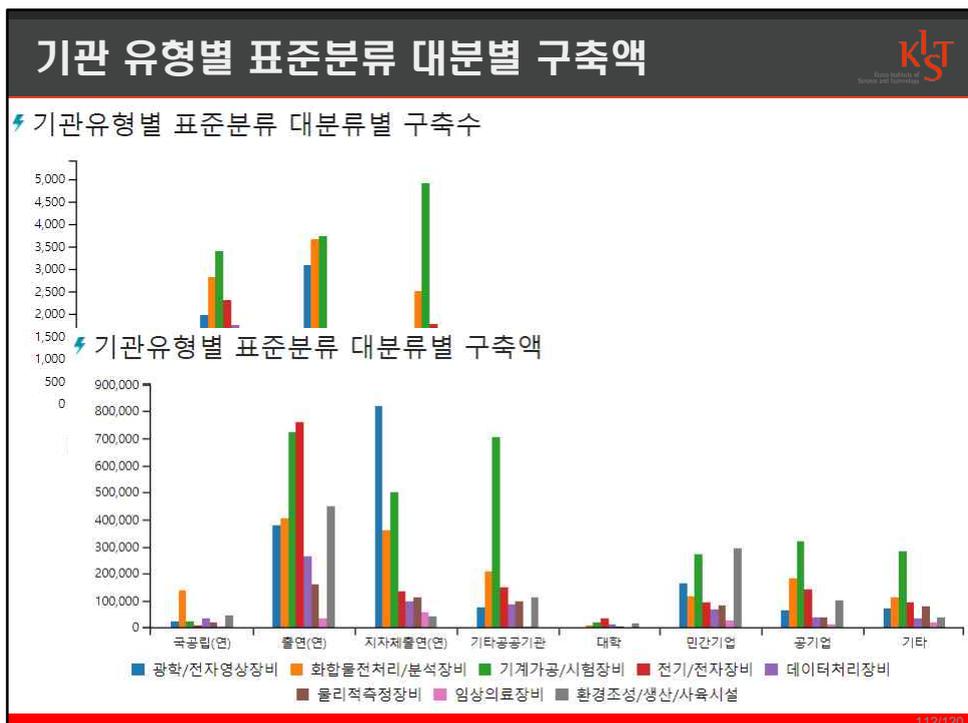
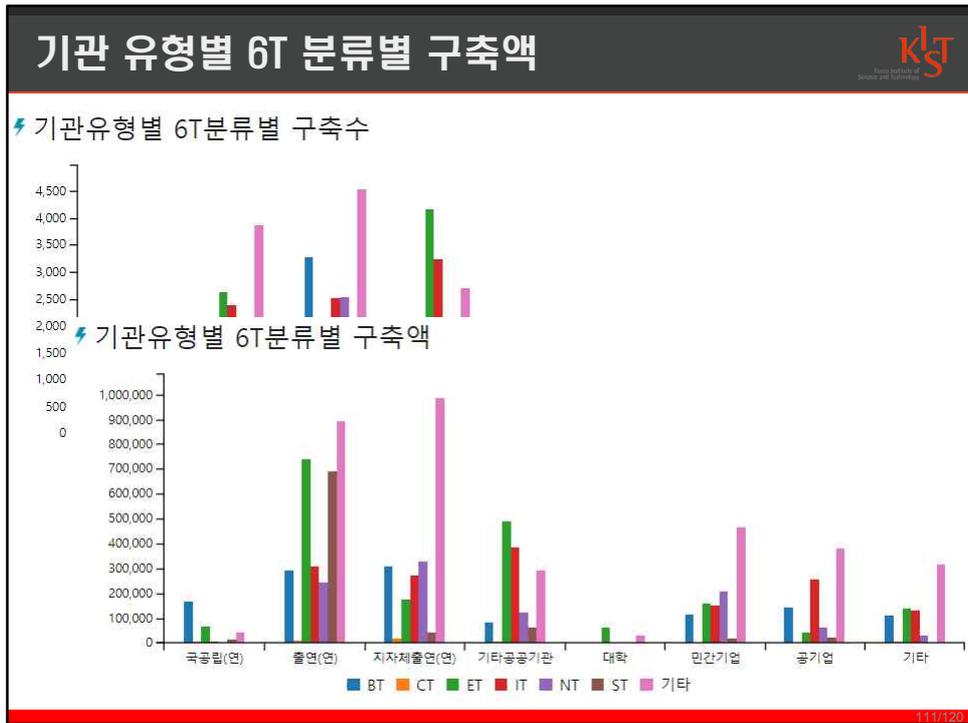


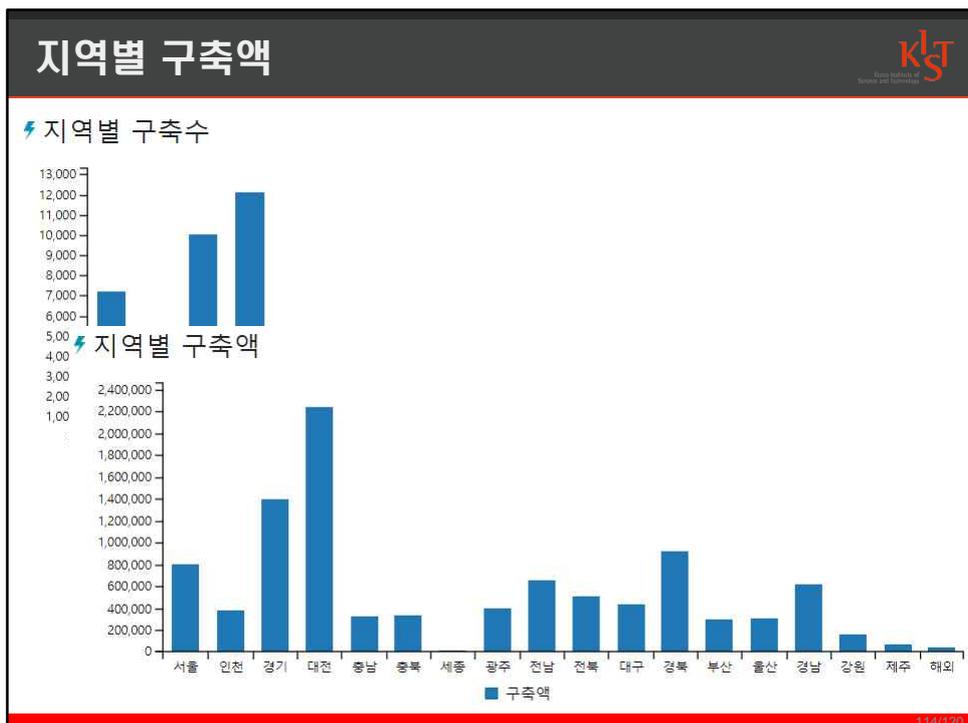
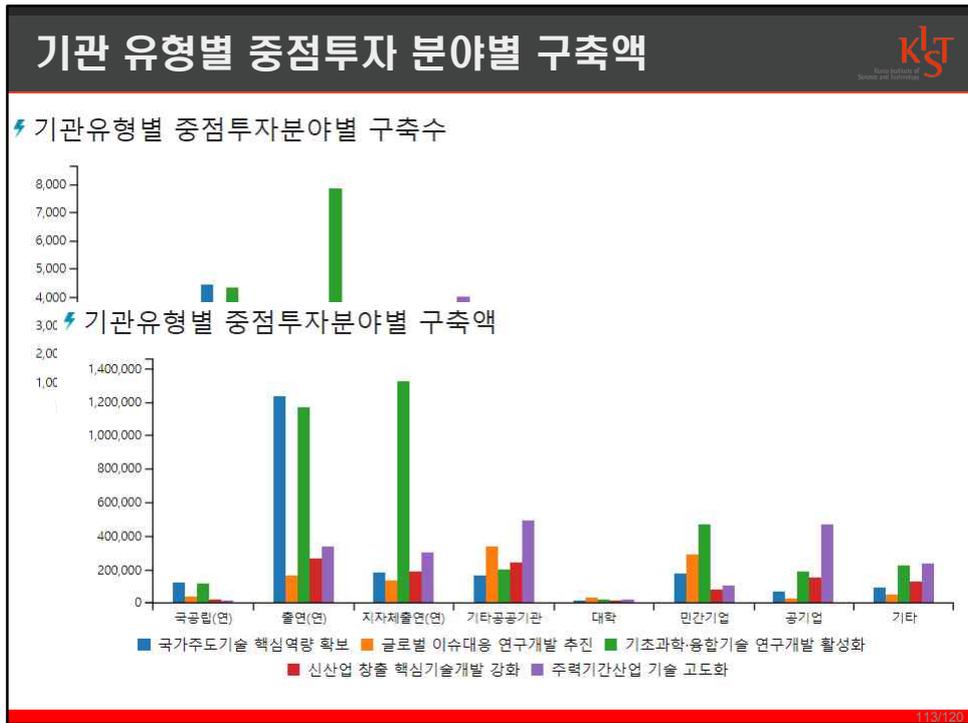


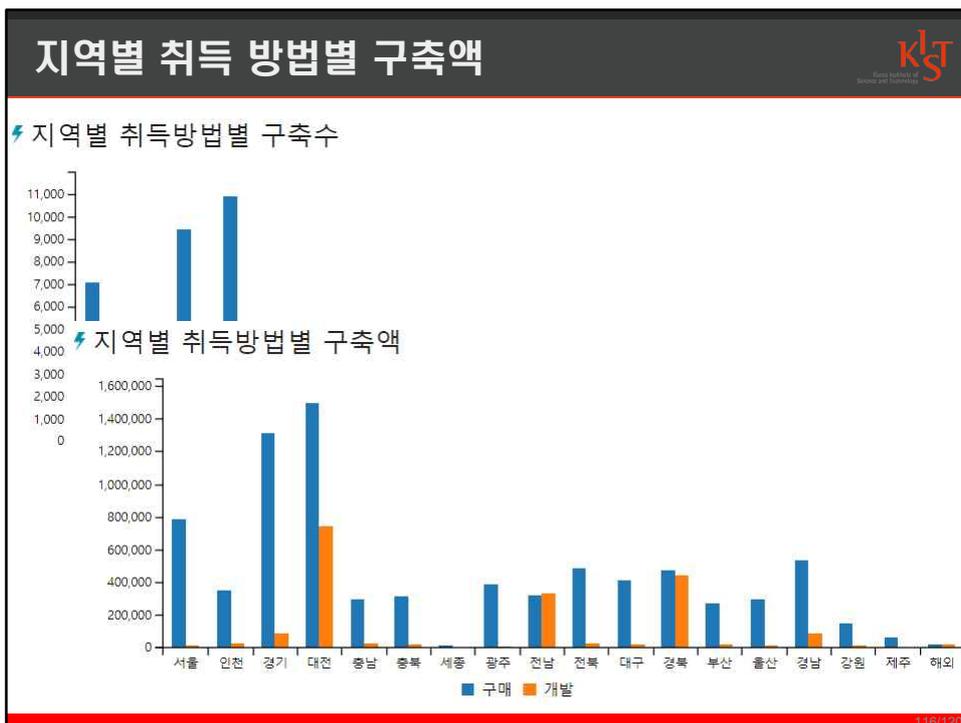
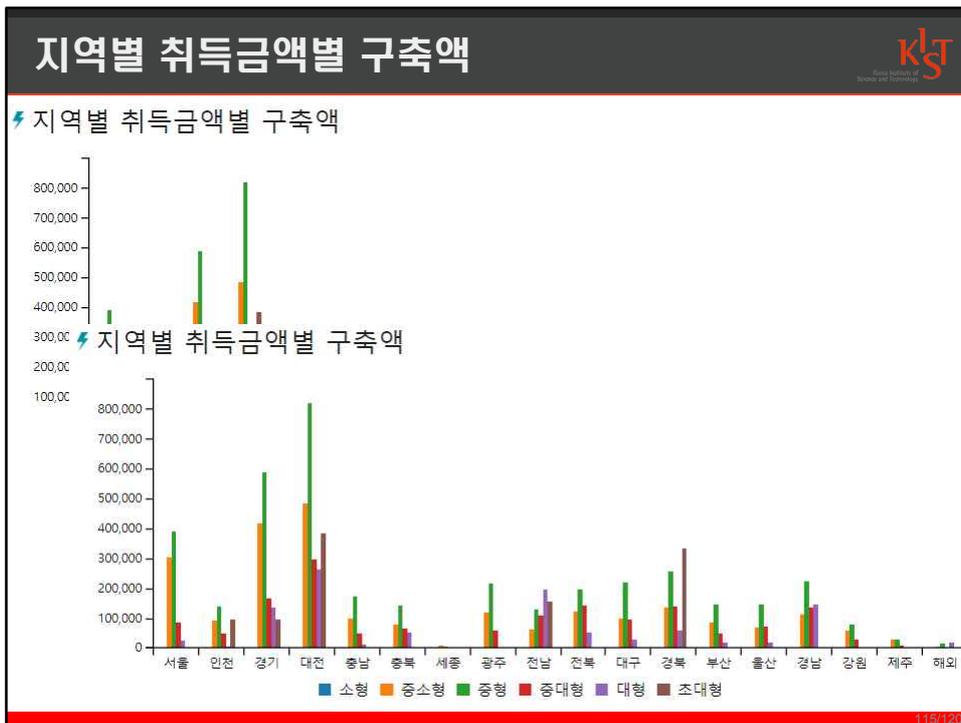


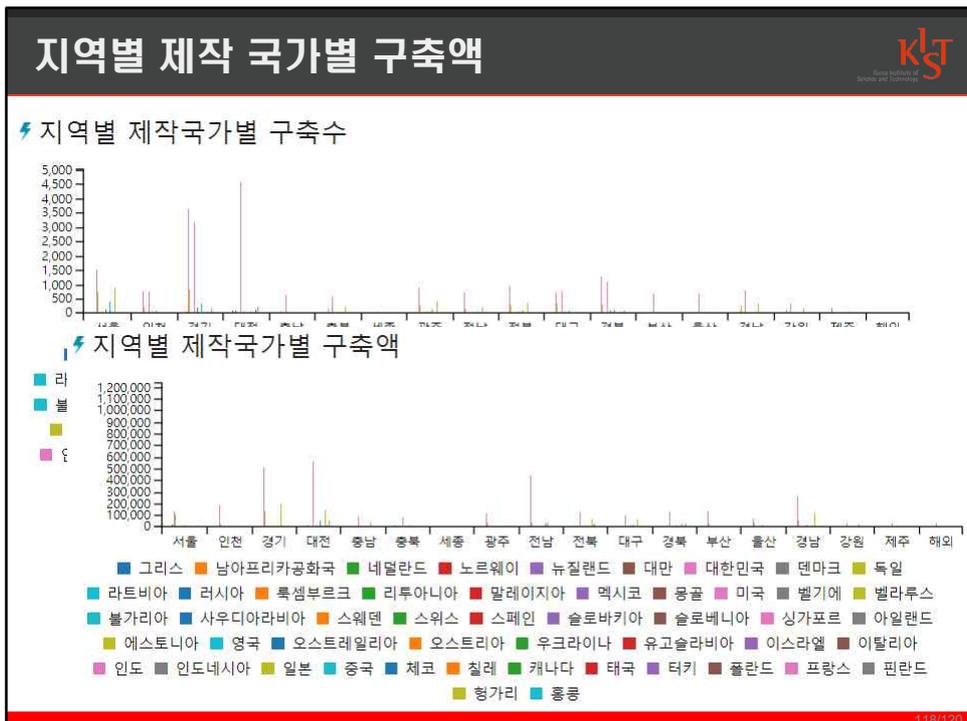
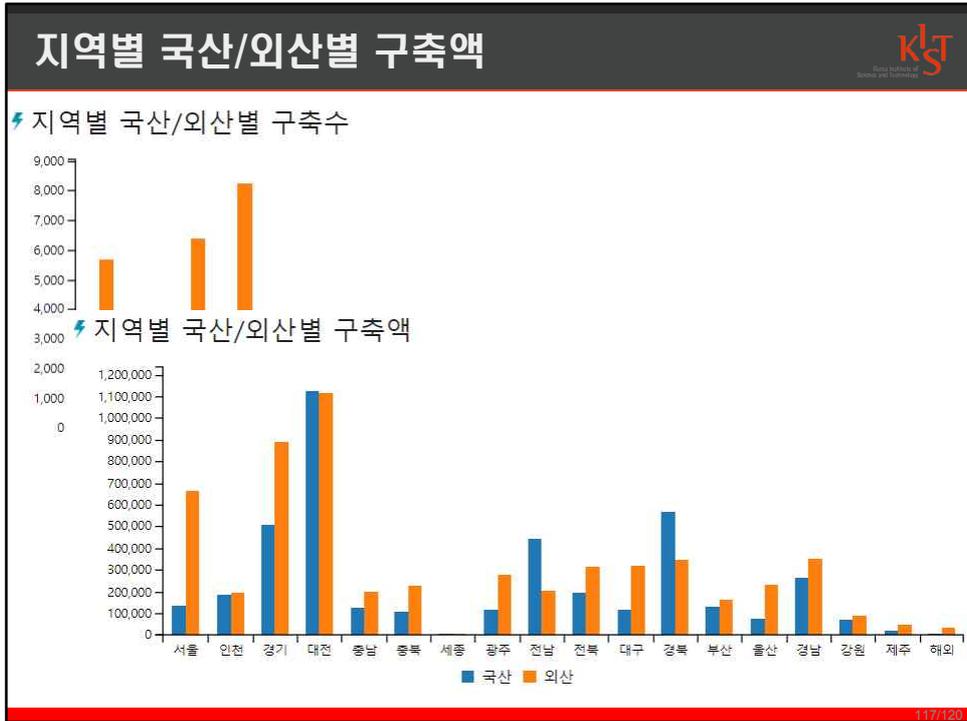


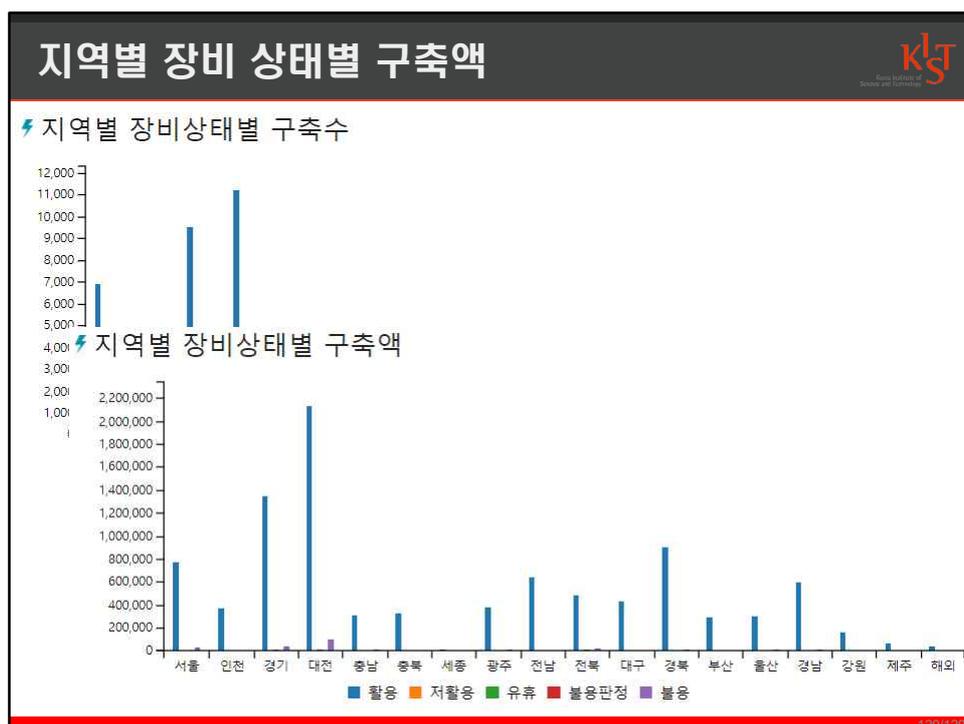
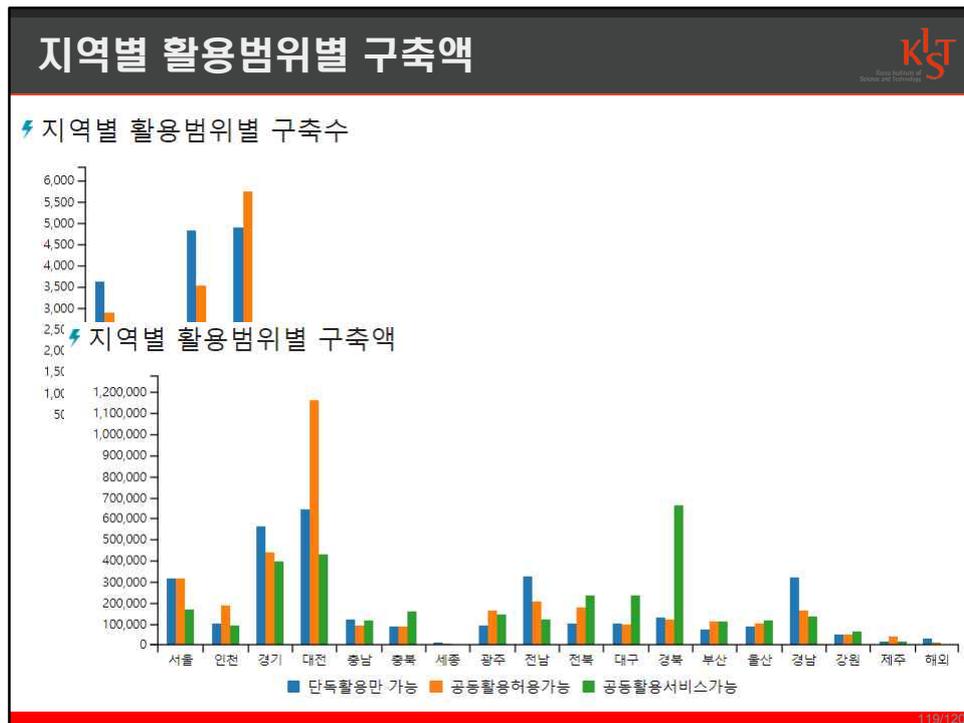


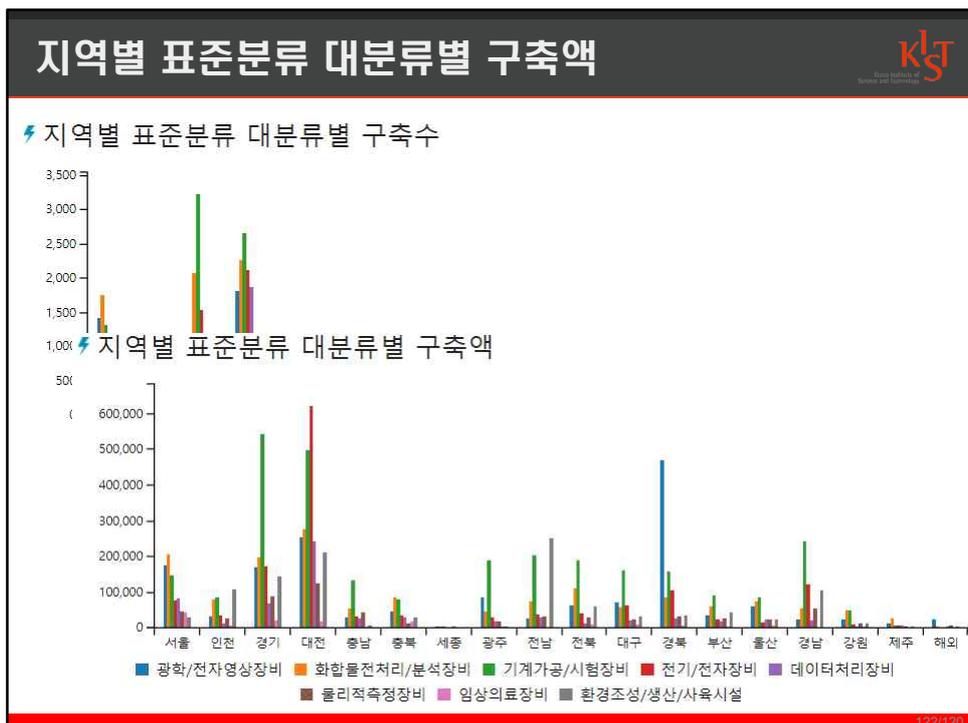
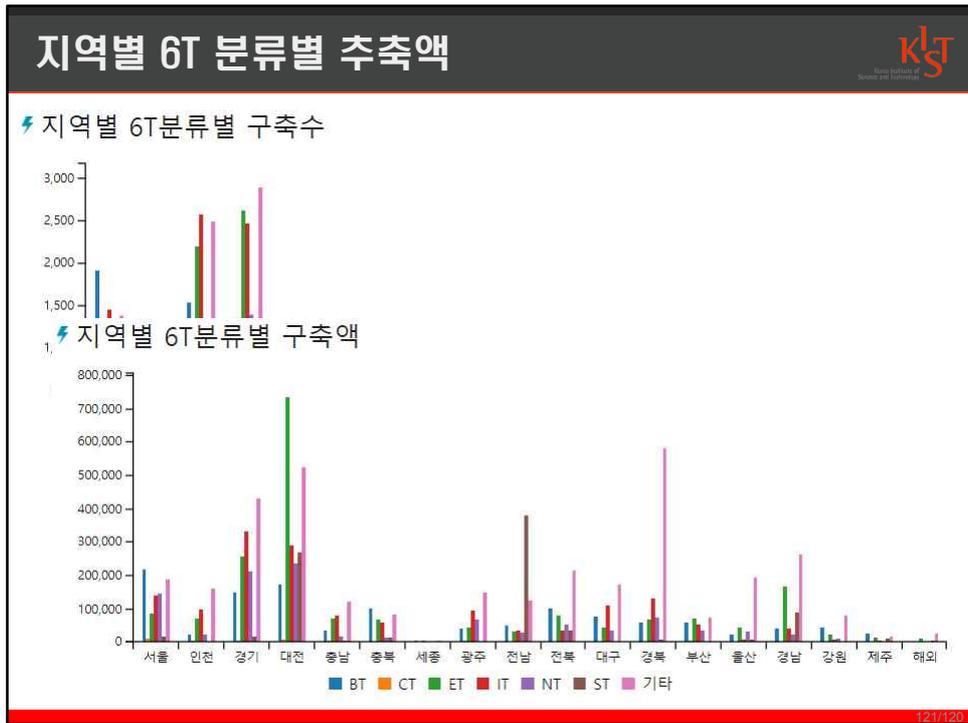


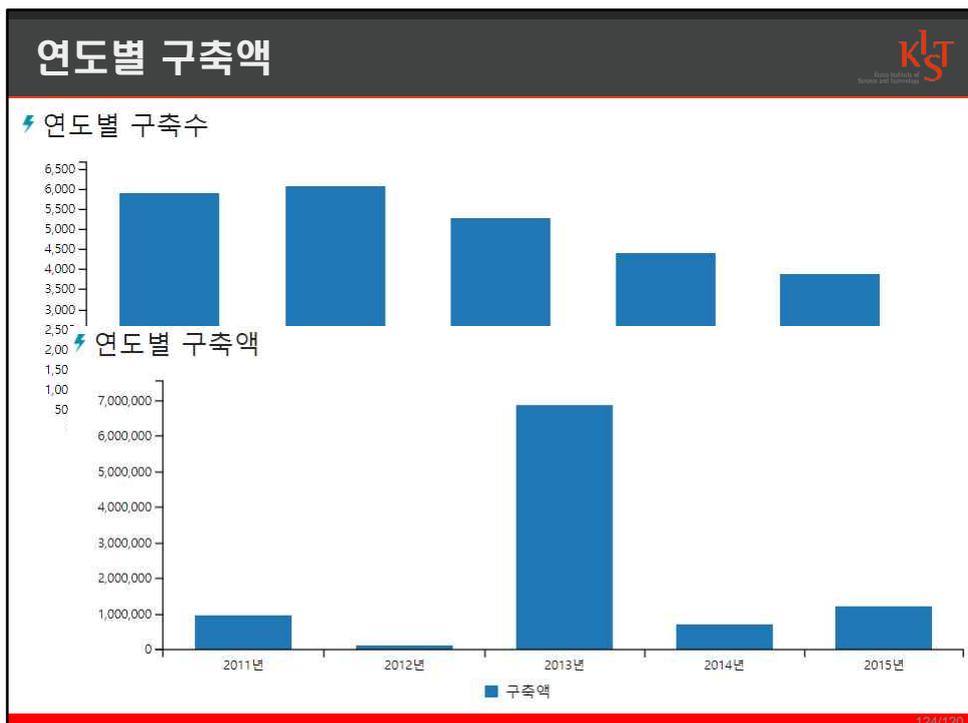
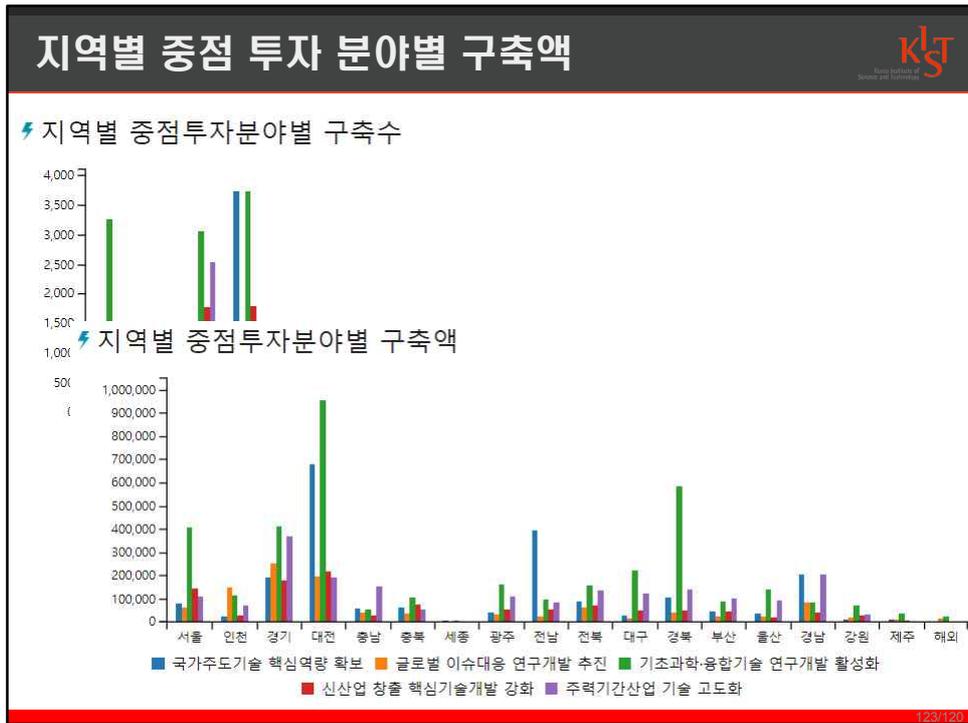


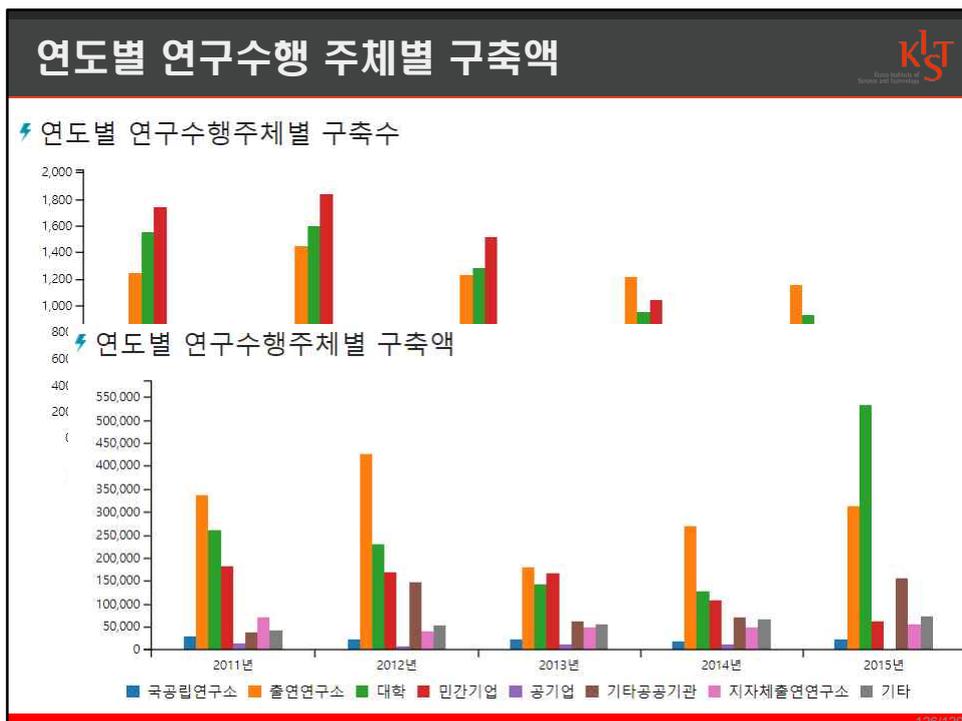
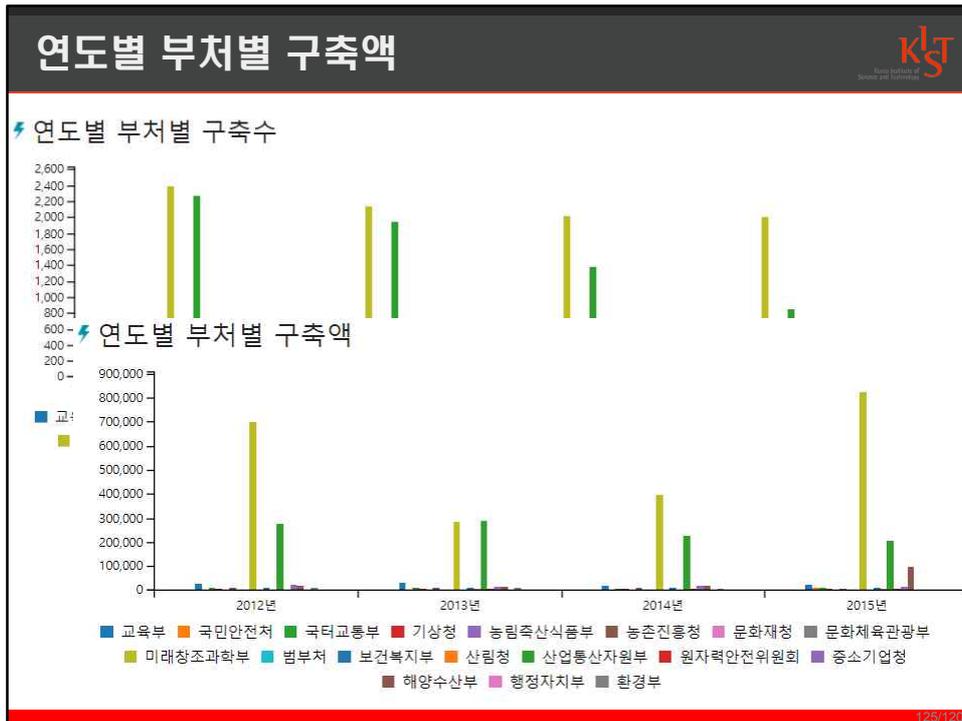


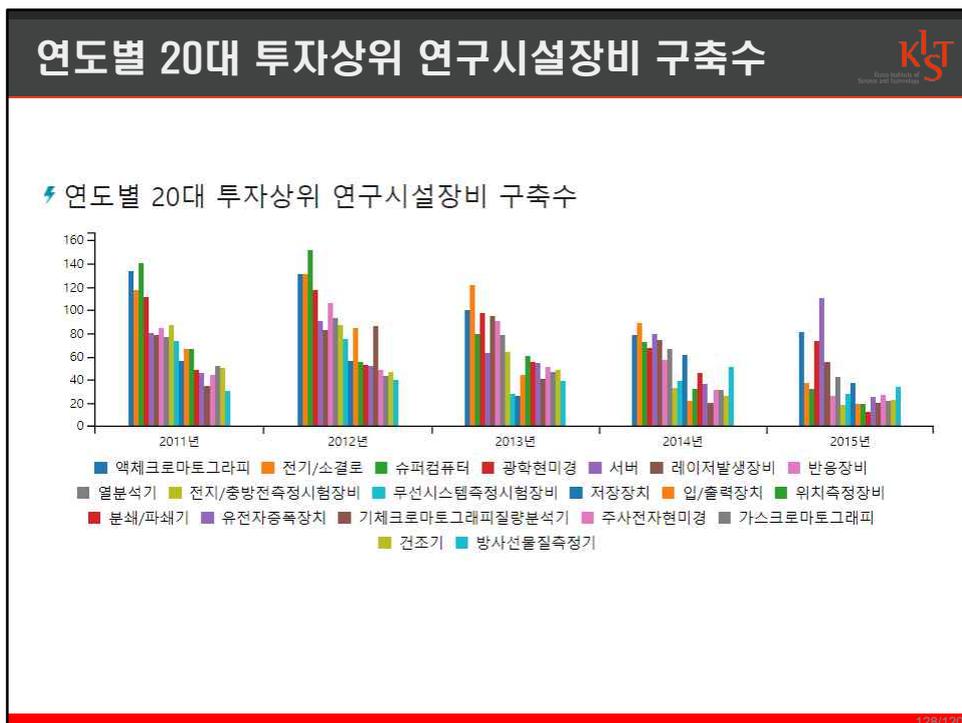
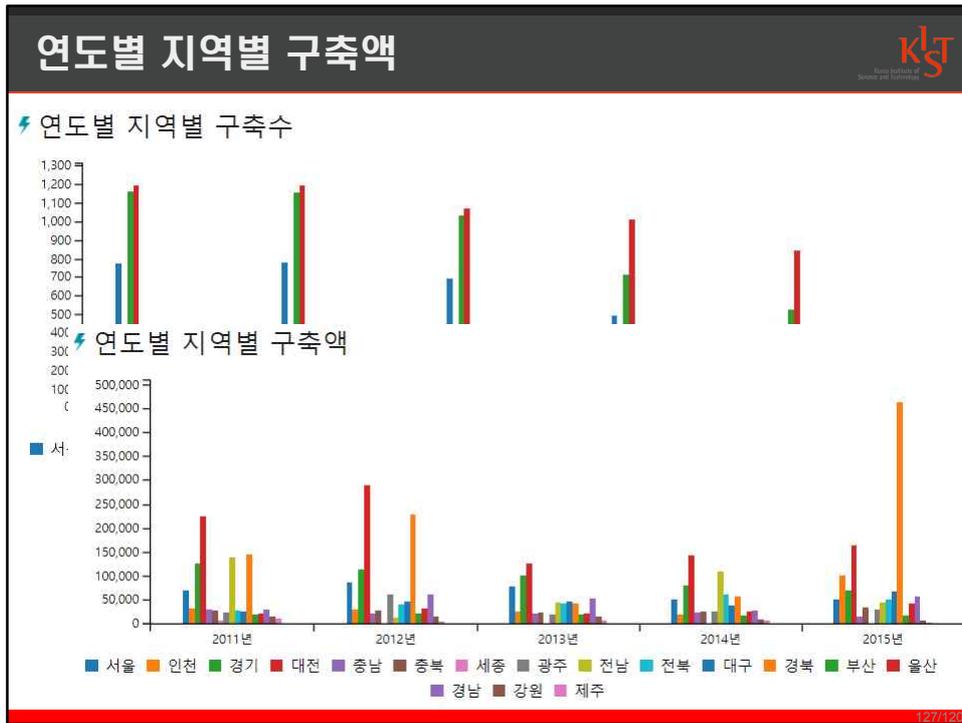


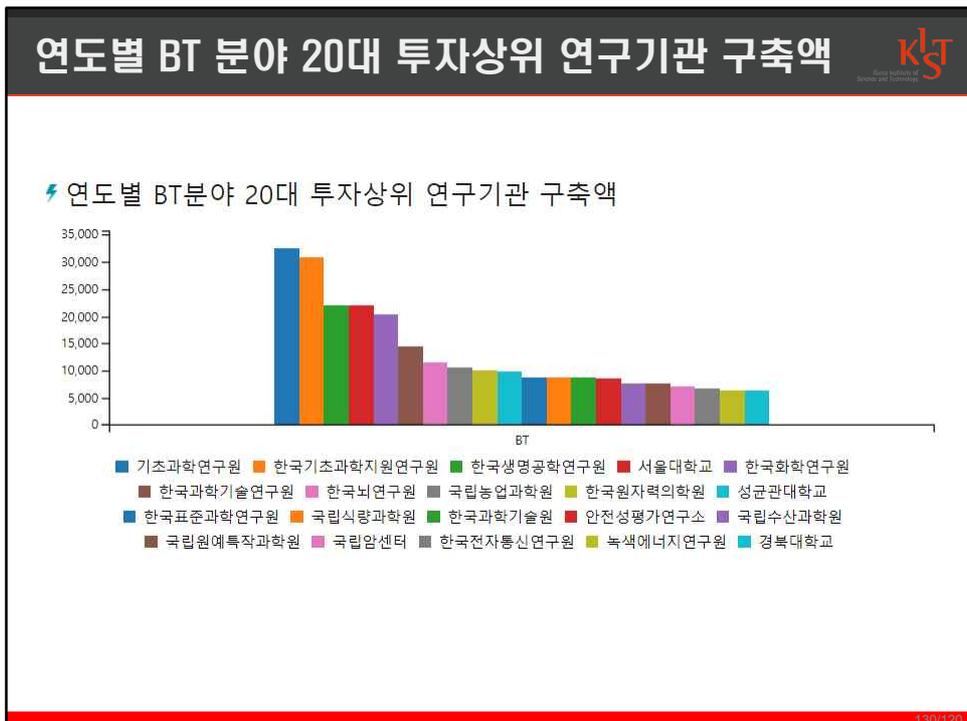
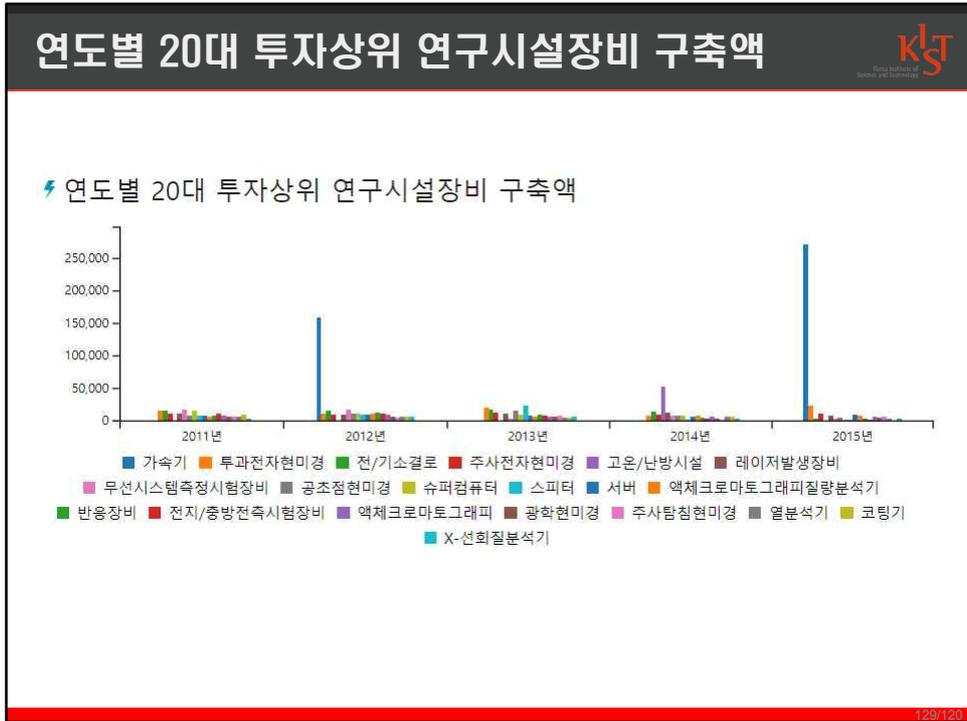


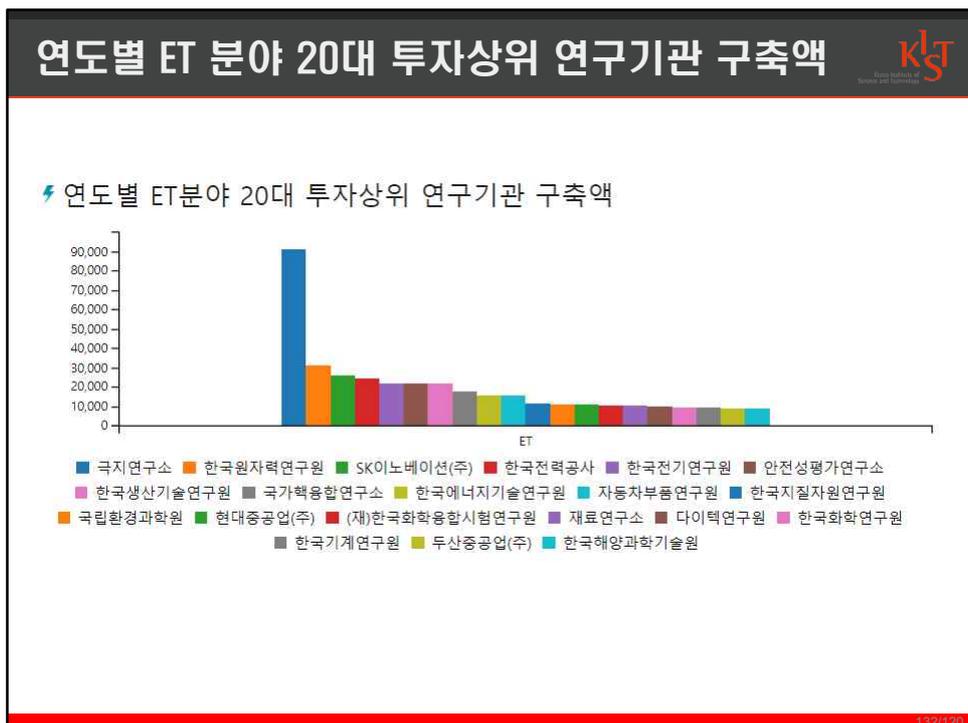
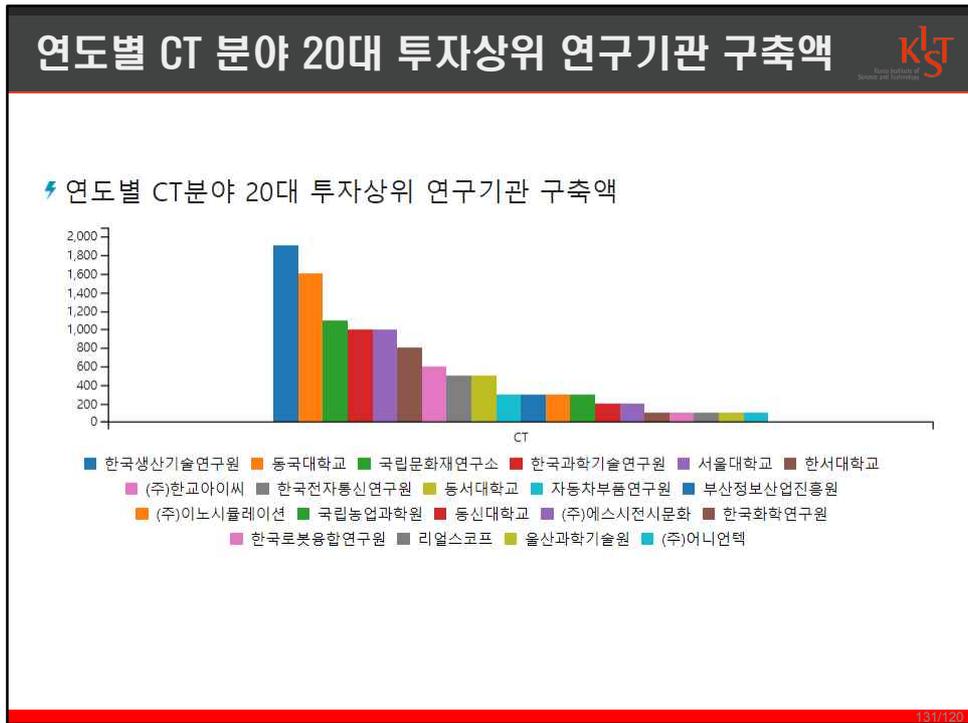


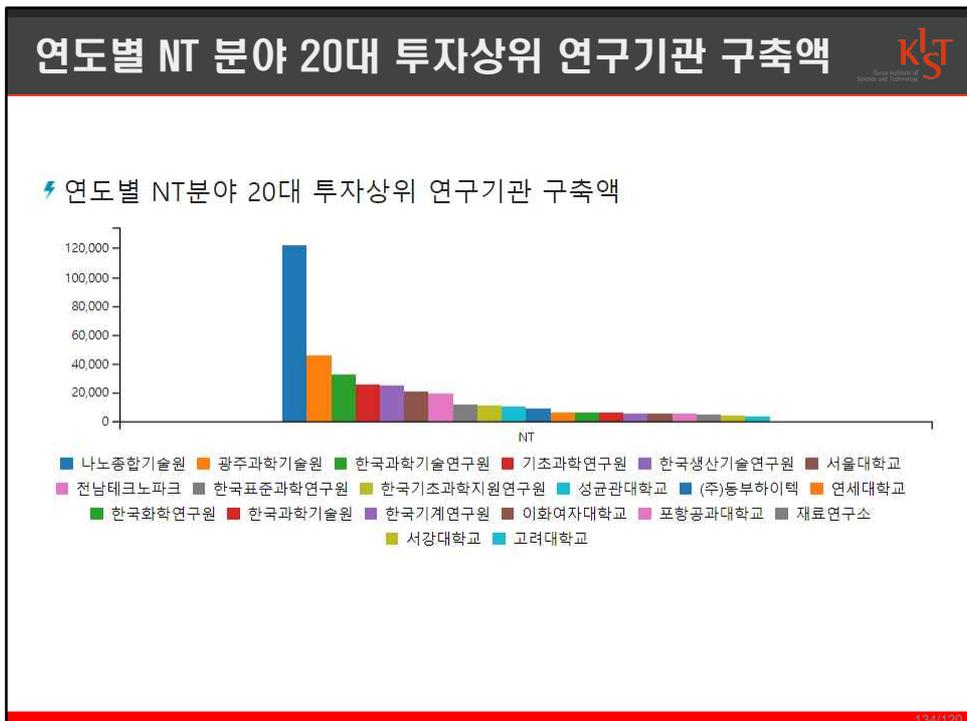
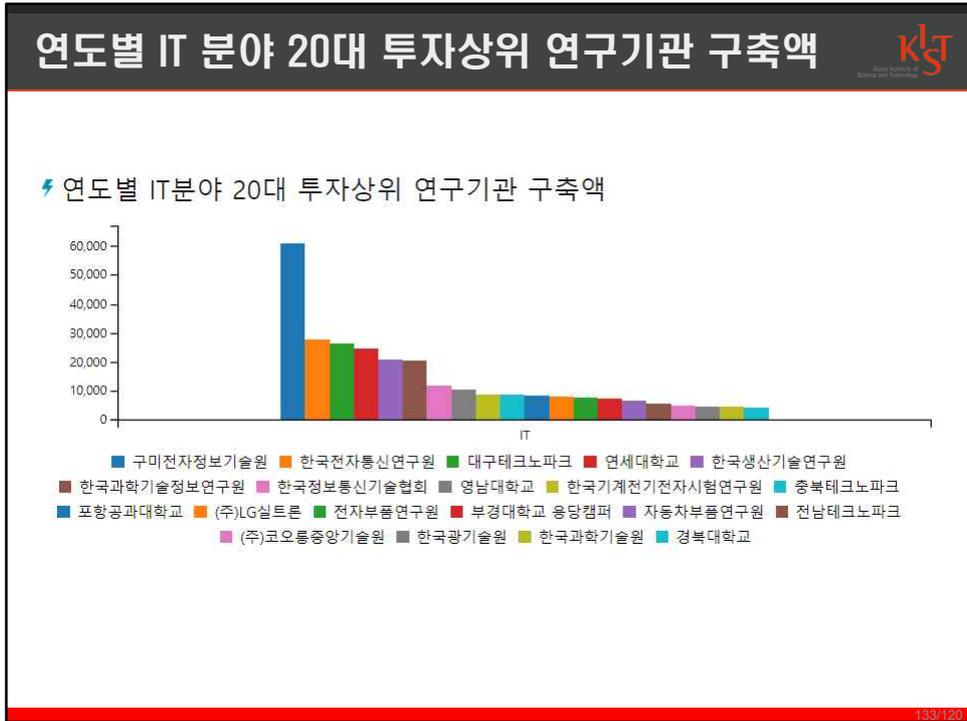


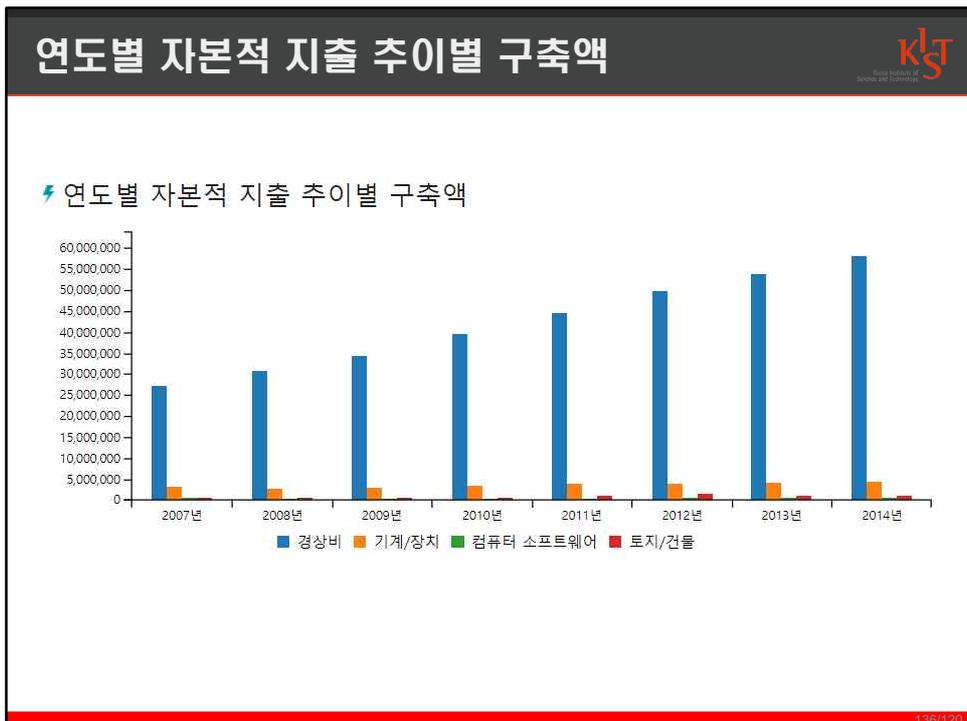
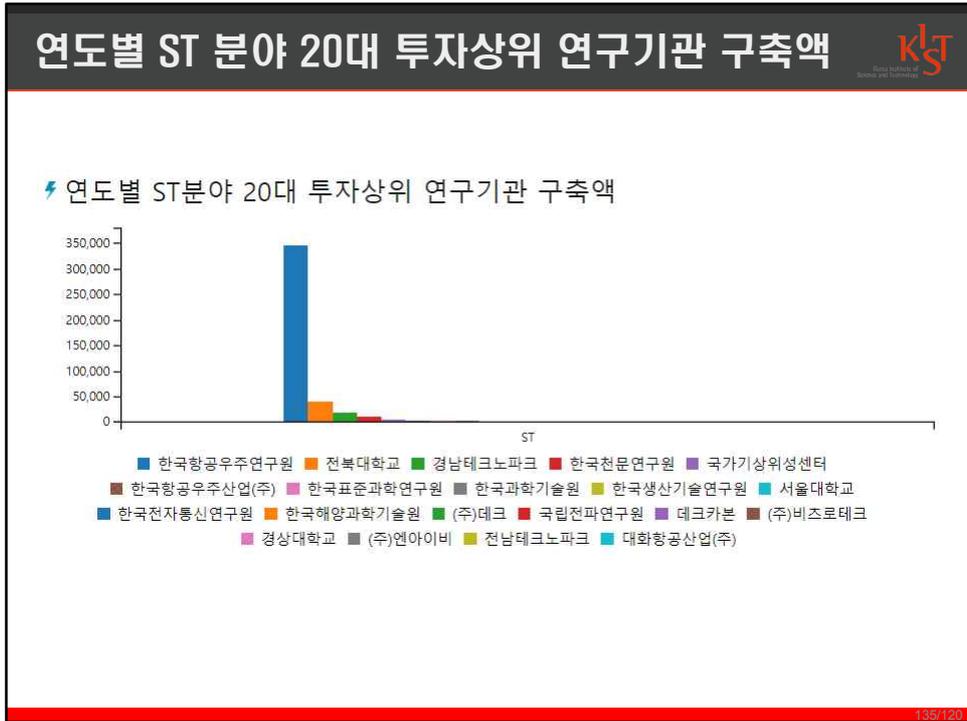


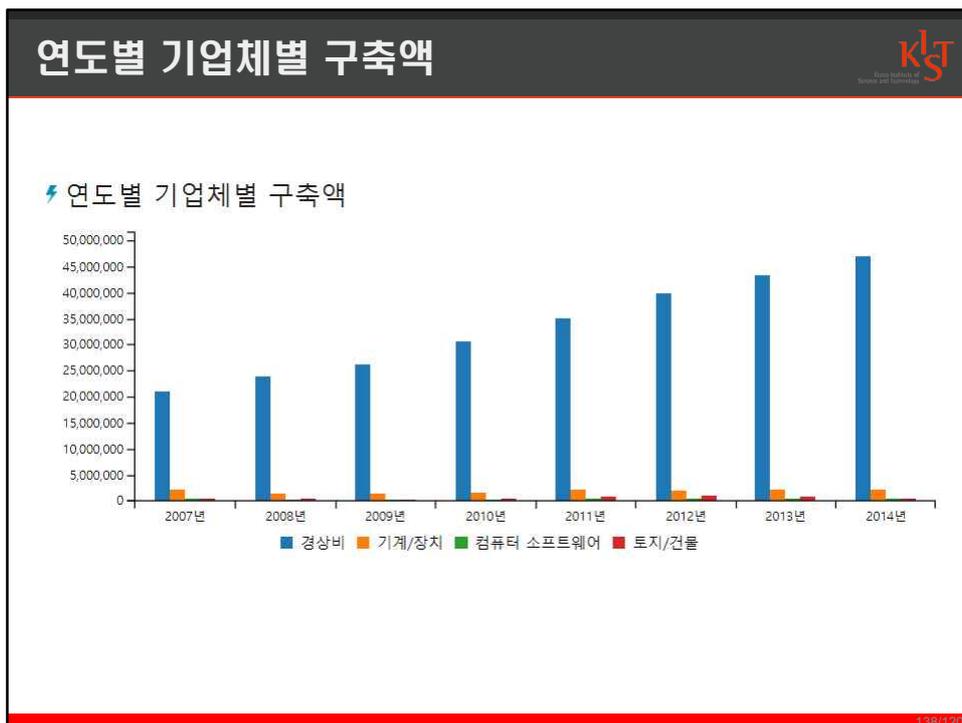
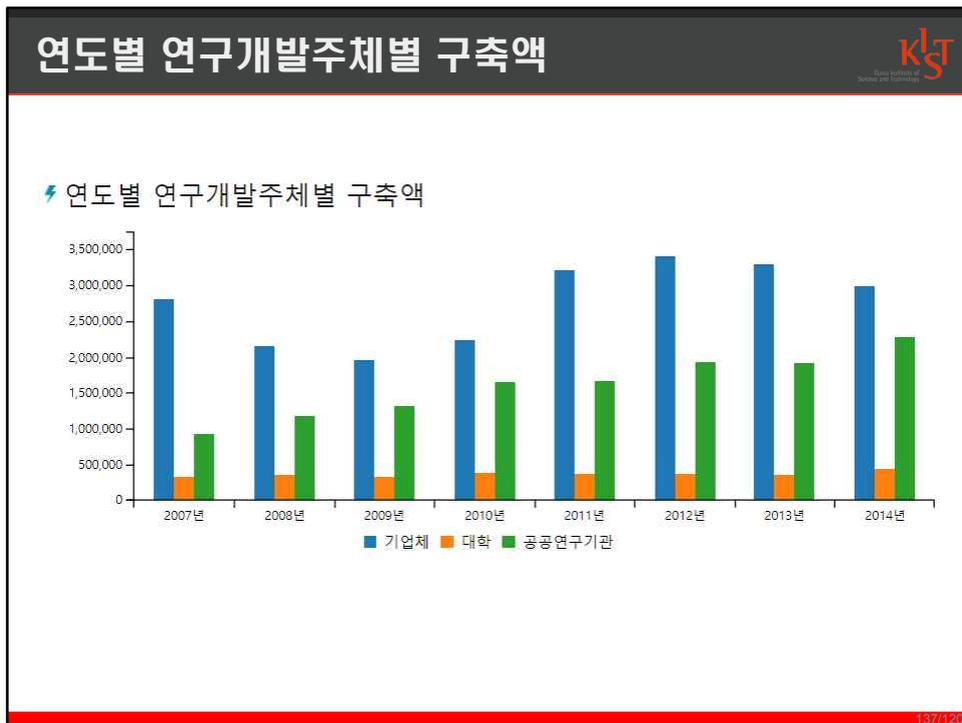


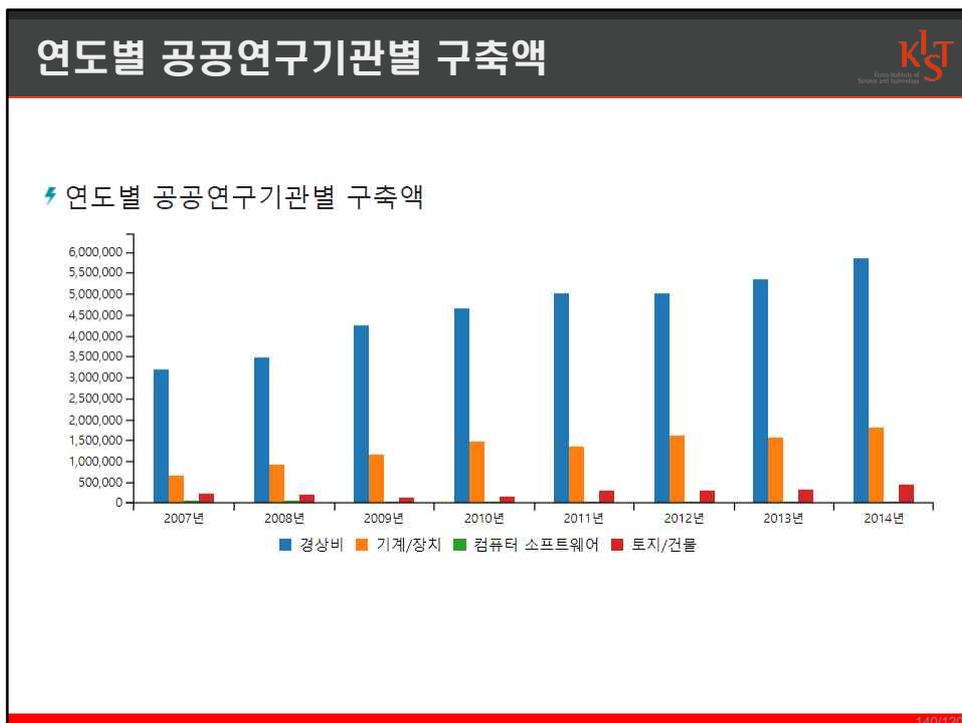
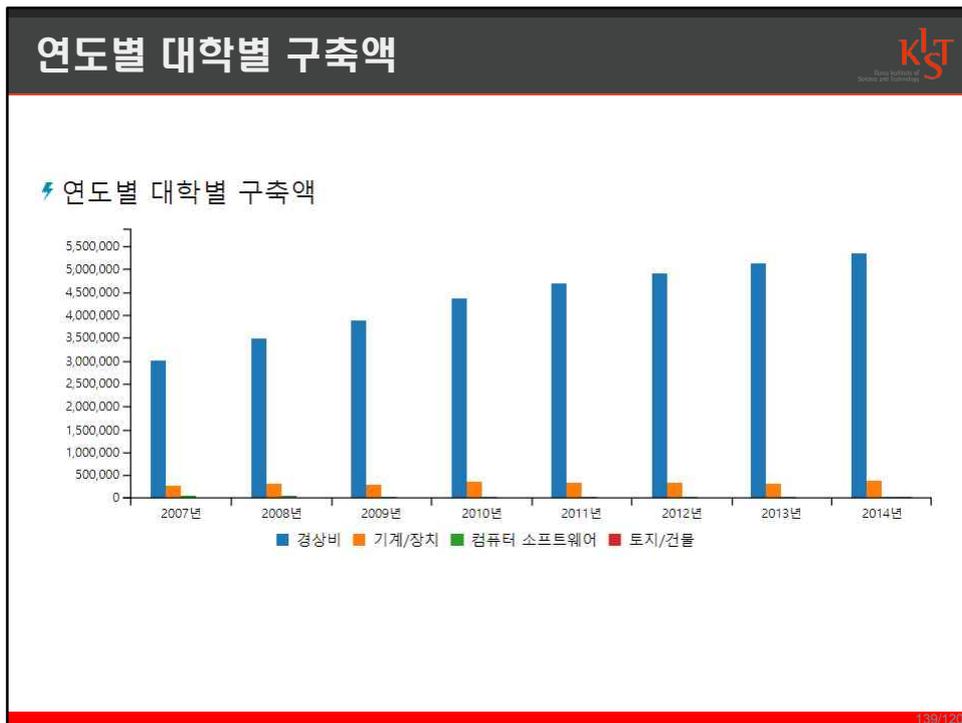












연도별 장비수



Korea Institute of Science and Technology

취득년도	장비구분	구매장비	개발장비	연구시설	Totals
2005		3,573	66	23	3,662
2006		4,038	60	22	4,120
2007		4,820	112	32	4,964
2008		4,986	152	29	5,167
2009		4,843	222	33	5,098
2010		4,507	308	39	4,854
2011		5,441	437	38	5,916
2012		5,540	487	46	6,073
2013		5,019	452	40	5,511
2014		4,001	418	48	4,467
2015		3,634	446	82	4,162
2016		3,104	241	109	3,454
2017		824	26	16	866
	Totals	54,330	3,427	557	58,314

141/120

연도별 장비 구축액



Korea Institute of Science and Technology

취득년도	장비구분	구매장비	개발장비	연구시설	Totals
2005		480,694,562,254	28,214,871,628	7,054,017,033	515,963,450,915
2006		537,588,817,852	19,582,792,660	21,170,699,680	578,342,310,192
2007		704,003,482,751	382,159,125,692	41,118,012,803	1,127,280,621,246
2008		696,163,547,951	39,125,353,919	27,919,277,170	763,208,179,040
2009		736,972,996,509	48,747,918,573	175,375,395,042	961,096,310,124
2010		569,153,953,728	78,578,296,308	8,946,939,932	656,679,189,968
2011		691,541,165,003	269,191,657,828	10,699,286,575	971,432,109,406
2012		680,970,941,804	77,127,481,179	10,709,554,696	768,807,977,679
2013		696,368,580,754	65,037,018,599	5,882,372,778	767,287,972,131
2014		528,605,661,284	86,816,677,960	92,621,072,369	708,043,411,613
2015		580,360,338,645	415,321,150,604	43,074,293,983	1,038,755,783,232
2016		581,869,381,223	55,133,984,290	154,765,088,991	791,768,454,504
2017		136,970,262,704	70,396,621,225	4,757,773,403	212,124,657,332
	Totals	7,621,263,692,462	1,635,432,950,465	604,093,784,455	9,860,790,427,382

142/120