vsparticle

Materials

Input

- Metals
- Alloys
- Metal oxides
- Semiconductors

H Hyaragon Lat	4 Be											В	c	7 N	8	9 F	2 He Herium 4
1 Ibnium 6 94 11 NB 50000m 22.99	12 Mg Magnesium 24.3											Boron 1081 33 Aluminium 26.98	Camon 122(1) 14 Silicon 28:09	Nitrogen 14.01 15 Prospnorus 30.97	16 Surrur 32.06	19 17 Cl Charine 35.45	N1997 2018 18 Argon 30.1
19 K Potzestani 39.95	20 Ca Califor 40.08	21 Scrimin 4495	22 11 11kan km .47.87	23 Varialosen 50.94	Chromium 52	25 Min Manganose 54.94	26. FC Iron 55/84	27 CO (0454) 58169	28 NI Nicker Saist	CU CU Copper 63.55	10 Zn 210: 65:39	61 Gallom 69.72	S2 Ge Seminium 7258	33 AS Arsenic 74.92	34 Se Secontari 78.96	35 Br Bramino 79.9	36 Kr Krypton 83.8
RD Romanim B5.47	36 Stronitum B7.62	39 Y Yitrauni BEL91	40 Zfr 21monuum 91.22	Nicosum 92.91	42 MO Maryoaemum ag saa	43 TC Technolium 98	RU Rutinentum 101.072	45 Rh Rhainm 107.91	AG PC Assortum 105.42	47 Ag Silver 107.87	IB CCI Caimmum 112,81	19 Incisium 114.82	50 Sn 110 (18.7)	ST SD Antimony 121.76	57 TC Texation 12639	53 kanine 127.6	54 Xenon 131.29
5 CS Cesture 132:91	BC BC Harium 137.33	57-71 Lantnanolos	77 Hf Hitourr -178.49	73 Ta Tantanum 180.95	V4 W Jungsten TRABA	75 Re Riterium 186.21	Ve OS Usmbm 190.23	77 LF Irlaium 192:22	20 Pt Patnum 195 08	79 AU 600 196:97	BO Hg Mercury 200.59	B1 TI Impanitum 204.38	82 PD Liser 207.2	83 Elsmon 208,98	84 Po Poentine 209	At Astatine 210	Rn Rn Ramin 272
Fr Handum 223	Ra Radum 226	89-103 Actinolos	104 Rf Rumentaria 262	105 DD Dutinium 262	105 Sg Scaborgium 264	Bh Bonnan 265	Hassion 268	109 Mt Melthorium 272	110 DS Darmstanniu 277	Rontgium	Copernicium 0	113 Nh Ninonium Q	114 Fil Fictovium Q	Mescavium 0	LVC	TS TS Immestee 0	tia Og Oganesar O
	Lanthanolds		5/ La Laninanoum 138391	SE Ce Cerium 140.12	59 PT Pasknaymi 140,91	no Nd Msoaymuum 144.24	F1 Pm Prometmium 145	Sm	EU EU Foroplom	64 GC Laooninium 157,25	IES TD Teratum 158.93	Dysproclum	E7. HO Hoimium 4164,93	56 Erotum 167.76	69 Tm Inuium 168,93	20 YD Viterinum 173.04	12 LU Lukelum 17497
	Actinolds		B9 AC Actinium 227	90 Th Inortum 231.04	91 Pa Protectinium 732.04	92 U	93 Np Neptonum 238.03	94 PU Potoniumi 243	95 Am Ameridam 244	96 Cm Curturs 247	97 BK Berkelum 247	98 Cf Camorium 251	99 ES Einsteintum 252	¹⁰⁰ Fm	101 Mchanachaint 258	102 NO	103 Lr Lawrenclus 261



Research interest

Edmontor



QUÉBEC

NEW

MASSACHUSETT







Proof of principle

7981

Technical

Volume 48, Number 25

PHYSICAL REVIEW LETTERS

21 JUNE 1982

• 3-16 nm C and Ag particles

Enormous Enhancement of van der Waals Forces between Small Silver Particles

Heinz Burtscher Laboratory for Solid State Physics, Eidgenossische Technische Hochschule, CH-8093 Zürich, Switzerland

and

Andreas Schmidt-Ott Atmospheric Physics and Laboratory for Solid State Physics, Eidgenossische Technische Hochschule, CH-8093 Zürich, Switzerland (Received 4 December 1981)

Dispersion forces enhance the coagulation rate of small particles in a gas. Measurements of coagulation rates on ultrafine Ag and C particles with radii of 3-16 nm were performed. The results obtained with C particles almost agree with the expectations based on bulk electronic properties. However, Ag particles 14 nm in radius exhibit a very large coagulation rate. It points to an enhancement of the dispersion forces of at least a factor of 10^4 .

Heinz Burtscher and Andreas Schmidt-Ott. Enormous enhancement of van der waals forces between small silver particles. *Phys. Rev. Lett.*, 48:1734–1737, Jun 1982.



First prototype

Technical



S Schwyn, E Garwin, and A Schmidt-Ott. Aerosol generation by spark discharge. Journal of Aerosol Science, 19(5):639 – 642, 1988.

Monodisperse output

- Deposition of charged silver particles
- Size selection based on electrical mobility

'9<u>9</u>.

• 8 nm deposited on carbon film





Fig. 1. TEM image of a carbon thin film covered with Ag particles. The particle diameter is 8 nm. The particle concentration is 120 particles per μm^2 after a sampling time of 2 h



B. Schleicher, Th. Jung, H. Hug, and H. Burtscher. Ultrafine particles adsorbed on hopg measured by stm. Zeitschrift für Physik D Atoms, Molecules and Clusters, 19(4):327–331, Mar 1991.

Clusters

Output

• Atomic clusters 1 – 40 Pd, Al atoms

7997

• Setup in vacuum

VS**particle**

②Dylec東京ダイレック株式会社



H. R. Siekmann, Ch. Lüder, J. Faehrmann, H. O. Lutz, and K. H. Meiwes-Broer. The pulsed arc cluster ion source (pacis). *Zeitschrift für Physik D Atoms, Molecules and Clusters*, 20(1):417–420, Mar 1991.

Output

Narrow size distribution for large particles

- Particle size distribution has a fixed width (1.27 < σ < 1.34)
- For large particles, the absolute spread is larger

199

• By continuously adding small NPs to the aerosol, the absolute width can remain constant (1 nm)



Themis Matsoukas and Erdogan Gulari. Self-sharpening distributions revisited—polydispersity in growth by monomer addition. *Journal of Colloid* and Interface Science, 145(2):557 – 562, 1991.

VS**particle**

①Dulec 東京ダイレック株式会社

First commercial spark generator

Technical



encies. Argon flow rate: $6.5 \ell \min^{-1}$, dilution a $21.0 \ell \min^{-1}$.

C. Helsper, W. Mölter, F. Löffler, C. Wadenpohl, S. Kaufmann, and G. Wenninger. Investigations of a new aerosol generator for the production of carbon aggregate particles. *Atmospheric Environment. Part A. General Topics*, 27(8):1271 – 1275, 1993.



Aerosol catalysis

• Methanation: $4 H_2 + CO_2 - > CH_4 + 2 H_2O$ using Ni

Table 1. Properties of the Ni aerosol catalyst before and after heating for 7 s at 450°C

Sampling location	Specific surface area (m ² /g)	Aerosol mass conc. (μg/cc)	Surf. conc. (BET) (cm ² /cc)	Surf. conc. (SMPS) (cm ² /cc)	Geom. mean diameter (nm)	Primary particle diam. (nm)
Before heating section	173.6	0.0799	0.1387	0.0650	144	3.9
Behind heating section	165.5	0.0465	0.0796	0.0429	103	4.1

7999



Figure 7. Arrhenius plot of the reaction rate for methanation on airborne Ni particles.

Alfred P. Weber, Martin Seipenbusch, Christoph Thanner, and Gerhard Kasper. Aerosol catalysis on nickel nanoparticles. *Journal of Nanoparticle Research*, 1(2):253–265, Jun 1999.



Application

Radiolabeling of carbon aerosol

Application



FIGURE 5. Specific activity of aerosol decreases as the sum of a fast and a slow exponential decay function of generator operation time. The half times for fast and slow generator output phases were 0.4 min and 4.8 min, respectively. Notations on curves are the electrode arcing frequency and activity applied to the electrodes.

 Application of radioactive Tc in liquid applied to spark electrodes

VS**particle ①**Dylec_東京ダイレック株式会社

James S. Brown, Chong S. Kim, Parker C. Reist, Kirby L. Zeman, and William D. Bennett. Generation of radiolabeled "soot-like" ultrafine aerosols suitable for use in human inhalation studies. Aerosol Science and Technology, 32(4):325-337, 2000.



Synthesis of oxides

Material



 Table 1

 Characteristics of ultrafine aerosols generated for various operation parameters of the generator

		Operation c	onditions		1	Particle characte	ristics	Mass-related surface area		Volume-related surface area	
	Discharge	Argon flow rate (lpm)	Nitrogen flow rate (lpm)	Air flow rate (lpm)	Modal diameter (nm)	Number concentration (cm ⁻³)	Mass concentration (µg m ⁻³)				
Particle material	frequency (Hz)							$\frac{\text{BET}_{\text{m}}}{(\text{m}^2 \text{ g}^{-1})}$	$\begin{array}{c} ASA_m \\ (m^2 g^{-1}) \end{array}$	$\frac{\text{BET}_{\text{v}}}{(\text{m}^2 \text{ cm}^{-3})}$	ASA_v (m ² cm ⁻³)
Carbon	3	6.3	17	170	25	10 ⁶	25	750	47	1425	90
Carbon	300	6.3	17	125	70	107	115	750	17	1425	32
Carbon	300	6.3	0	125	150	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Silver	300	3.5	0	125	20	3×10^{6}	133	20	11	210	115
Iridium	140	6.3	0	125	18	2.5×10^{6}	83	n.a.	n.a.	n.a.	n.a.
Iridium	500	6.3	0	125	22	3×10^{7}	480	123	5.1	2766	102
Ferric oxide	20	5.4	17	165	35	106	40	300	10	1560	57
Cadmium oxide	6	3.5	17	165	35	106	65	50	9.2	408	75
Cadmium oxide	300	3.5	17	125	50	8×10^{6}	420	n.a.	n.a.	n.a.	n.a.



C. Roth, G. A. Ferron, E. Karg, B. Lentner, G. Schumann, S. Takenaka, and J. Heyder. Generation of ultrafine particles by spark discharging. *Aerosol Science and Technology*, 38(3):228–235, 2004.

VS**particle**

①Dylec 東京ダイレック株式会社

Synthesis of titania by sparking in air

Material





Hyun Cheol Oh, Jun Ho Ji, Jae Hee Jung, and Sang Soo Kim. Synthesis of titania nanoparticles via spark discharge method using air as a carrier. In *Eco-Materials Processing and Design VIII*, volume 544 of *Materials Science Forum*, pages 143–146. Trans Tech Publications, 5 2007.

XRD studies

- 10 20 nm particles
- Collection by filtration







L. Simonin, U. Lafont, N. Tabrizi, A. Schmidt-Ott, and E.M. Kelder. Sb/o nano-composites produced via spark discharge generation for li-ion battery anodes. *Journal of Power Sources*, 174(2):805 – 809, 2007. 13th International Meeting on Lithium Batteries.

Output

Influence of nanoparticle material of size distributions

Output

• Precious metals in N₂ gas

VS**particle**

①Dylec 東京ダイレック株式会社

 High production rates give higher concentrations and larger particles (Au > Pt > Pd > Ag)



Jeong Hoon Byeon, Jae Hong Park, and Jungho Hwang. Spark generation of monometallic and bimetallic aerosol nanoparticles. *Journal of Aerosol Science*, 39(10):888 – 896, 2008.

Patterning with metal catalyst particles

Patterning

- Pt particles in N₂ gas
- 5 min deposition using thermophoresis (ΔT)

VS**particle**

①Dulec 東京ダイレック株式会社





Jeong Hoon Byeon, Jae Hong Park, Ki Young Yoon, and Jungho Hwang. Site-selective catalytic surface activation via aerosol nanoparticles for use in metal micropatterning. *Langmuir*, 24(11):5949–5954, 2008.

Influence of carrier gas and various metals

Material

- Gases have various breakdown voltages changing the energy delivered to the spark
- Materials have different ablation rates depending on:
 - Thermal conductivity
 - Evaporation enthalpy
 - Boiling point

VS**particle**

②Dylec東京ダイレック株式会社

N. S. Tabrizi, M. Ullmann, V. A. Vons, U. Lafont, and A. Schmidt-Ott. Generation of nanoparticles by spark discharge. *Journal of Nanoparticle Research*, 11(2):315, May 2008.



 Table 1 Gold particle sizes under various conditions

	N_2		Ar		Не		
P (atm)	1	2	1	2	1	2	
$d_{\rm g}$ (nm)	7.0	5.5	4.7	4.7	4.0	4.1	
$\sigma_{\rm g}$	1.34	1.35	1.42	1.37	1.45	1.4	
Count	35	37	40	44	69	36	



Carbon encapsulation

VS**particle**

①Dylec_東京ダイレック株式会社

Output



Jeong Hoon Byeon, Jae Hong Park, Ki Young Yoon, and Jungho Hwang. Ambient spark generation to synthesize carbon-encapsulated metal nanoparticles in continuous aerosol manner. *Nanoscale*, 1:339–343, 2009.

Producing alloyed electrodes

Material



VS**particle ②Dylec**東京ダイレック株式会社 Ugo Lafont, Loïc Simonin, Nooshin S. Tabrizi, Andreas Schmidt-Ott, and Erik M. Kelder. Synthesis of nanoparticles of cu, sb, sn, snsb and cu2sb by densification and atomization process. Journal of Nanoscience and Nanotechnology, 9(4):2546-2552, 2009.

Fig. 8. (a) XRD pattern of the Cu-Sb sample before compaction (bottom, black), after compaction (middle, blue) and after atomization (top, red). # Sb phase, o Cu phase and ×Cu₂Sb phase. (b) XRD pattern of the Sn-Sb sample before compaction (bottom, black), after compaction (middle, blue) and after atomization (top, red). # Sn phase, + Sb phase and * SnSb phase.

VS**particle**

①Dulec 東京ダイレック株式会社

Using nanoparticles as seeds for epitaxial growth

Application

Deposition by electrostatic precipitation

tube furnace

Figure 4

TEM micrographs of (a) agglomerate gold particles and gold particles

reshaped at (b) 300°C (c) 600°C (d) 1200°C in a special compaction



SEM micrograph of (a) epitaxial GaP nanowires seeded with 20 nm gold particles, reshaped at 600°C, at a growth temperature of 460°C. The particle density was 1 μ m². (b) epitaxial InP nanowires seeded with 30 nm gold particles, reshaped at 600°C, at a growth temperature of 420°C. The particle density was 3 μ m². Images were acquired with the sample tilted (a) 52° (b) 30° towards the e-beam

Maria E. Messing, Kimberly A. Dick, L. Reine Wallenberg, and Knut Deppert. Generation of size-selected gold nanoparticles by spark discharge for growth of epitaxial nanowires. *Gold Bulletin*, 42(1):20–26, Mar 2009.



Study of model catalysts using aerosol deposition

• Size selected Pd nanoparticles

• Deposition on Si by electrostatic precipitation

Application



5070



Maria E. Messing, Rasmus Westerström, Bengt O. Meuller, Sara Blomberg, Johan Gustafson, Jesper N. Andersen, Edvin Lundgren, Richard van Rijn, Olivier Balmes, Hendrik Bluhm, and Knut Deppert. Generation of pd model catalyst nanoparticles by spark discharge. *The Journal of Physical Chemistry C*, 114(20):9257–9263, 2010.

①Dylec_東京ダイレック株式会社

Metallic nanoparticles from immiscible metals





of mixed metallic nanoparticles from immiscible metals by spark discharge. Journal of Nanoparticle Research, 12(1):247-259, Jan 2010.

Semiconducting nanoparticles

Material

 Doping decreases electrical resistivity (0.17 Ω cm) 10¹⁵ boron atoms/cm³



Fig. 5 a Photographs of an intrinsic silicon discharge.



Fig. 7 a Discharge voltage and current for boron-doped Si rods in 1.6 SLM Ar 5.0, 2 mm gap spacing. b photograph of the spark discharge between doped rods

Vincent A. Vons, Louis C. P. M. de Smet, David Munao, Alper Evirgen, Erik M. Kelder, and Andreas Schmidt-Ott. Silicon nanoparticles produced by spark discharge. *Journal of Nanoparticle Research*, 13(10):4867, Jun 2011.



Deposition of uniform layers

Output

- Deposition of Ag nanoparticles by diffusion
- Annealing at 300 C for 30 min
- Layer height of 104 nm
- Surface roughness of 8.7 nm



VS**particle** ^①Dylec_東京ダイレック株式会社

Jeong Hoon Byeon and Jang-Woo Kim. Fabrication of a pure, uniform electroless silver film using ultrafine silver aerosol particles. *Langmuir*, 26(14):11928–11933, 2010.

Production of highly oxidizing metals

Material

- Production of Mg nanoparticles
- Purification of 5N Ar: 5 ppm H₂O, O₂
- Bake-out of the system

VS**particle**

②Dylec東京ダイレック株式会社

• Preloading of the system with Mg NPs



Fig. 4. XRD patterns of Mg nanoparticles after background substraction: (a) as-produced; (b) after hydrogen loading (black, measured spectrum; red, Rietveld analysis; blue, residual of the fit). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

V.A. Vons, A. Anastasopol, W.J. Legerstee, F.M. Mulder, S.W.H. Eijt, and A. Schmidt-Ott. Low-temperature hydrogen desorption and the structural properties of spark discharge generated mg nanoparticles. *Acta Materialia*, 59(8):3070 – 3080, 2011.



VS**particle**

①Dylec_東京ダイレック株式会社

Size selected deposition of Au, Ge

Output



Fig. 4.7 a Bright field TEM images of Au nanoparticles of geometric mean diameter of 9.87 nm, b size distribution by SMPS measurement and c size distribution calculated by TEM images



Fig. 4.10 a TEM image of Ge nanoparticles, obtained after sintering at 900 $^{\circ}$ C, b size distribution as monitored by SMPS and c size distribution obtained by TEM images analysis

Shubhra Kala, Marcel Rouenhoff, Ralf Theissmann, and Frank Einar Kruis. Synthesis and Film Formation of Monodisperse Nanoparticles and Nanoparticle Pairs, pages 99–119. Springer Berlin Heidelberg, Berlin, Heidelberg, 2012.



VS**particle**

①Dylec_東京ダイレック株式会社

Writing by electrostatic focussing

Patterning



E. Saleh, M. Praeger, A. S. Vaughan, W. Stewart, and W. H. Loh. The direct writing and focusing of nanoparticles generated by an electrical discharge. *Journal of Nanoparticle Research*, 14(11):1220, Oct 2012.

VS**particle**

①Dylec_東京ダイレック株式会社

Effect of different configurations

 Configurations have different electrical fields and gas flow profiles



Fig. 1. Two different configurations of spark discharge generator. (A) Pin-to-plate type electrode configuration. (B) Rod-to-rod type electrode configuration.

Kyuhee Han, Woongsik Kim, Jiwon Yu, Jeonghoon Lee, Heechul Lee, Chang Gyu Woo, and Mansoo Choi. A study of pin-to-plate type spark discharge generator for producing unagglomerated nanoaerosols. *Journal* of Aerosol Science, 52:80 – 88, 2012.

Applied setting voltage (kV) 4.0x10 pin-to-plate configuration rod-to-rod configuration 3.5x10 Position '0' Position '1' 3.0x10 Position '0' 2.5x10 Position '1' 2.0x10 1.5x10 1.0x10 5.0x10 0.0 0.8 0.0 0.2 0.4 0.6 1.0 Normalized position

В

Electric field strength (V/m)

Technical

High stability by thiol capping of Au NPs



Production of large spherical particles

 Particles > 10 nm tend to agglomerate

VS**particle**

①Dylec_東京ダイレック株式会社

 Higher temperature increases mobility and produces spherical particles



FIG. 2. TEM micrographs of the Pd, Ag, and Pd-Ag alloy nanoparticles sintered at RT, 300 °C, 500 °C, and 700 °C.

Saurabh K. Sengar, B. R. Mehta, and Govind. Size and alloying induced changes in lattice constant, core, and valance band binding energy in pd-ag, pd, and ag nanoparticles: Effect of in-flight sintering temperature. *Journal of Applied Physics*, 112(1):014307, 2012.

Titania nanoparticles for photocatalysis

Scheme 1. Continuous Gas-Phase Self-Assembly of Graphene Nanoflakes with TiO₂ Nanoparticles for Photocatalytic Applications; Other Nanoparticles (ZnO, Au, and Ag) were Also Incorporated with Graphene Nanoflakes via the Same Method

- Spark ablation under air stream
- Deposition on graphene

VSparticle

①Dulec 東京ダイレック株式会社



Jeong Hoon Byeon and Young-Woo Kim. Gas-phase self-assembly of highly ordered titania@graphene nanoflakes for enhancement in photocatalytic activity. ACS Applied Materials & Interfaces, 5(9):3959–3966, 2013.

Antibacterial silver coatings on HEPA filters

- Dust captured in filters can serve as nutrients for bacteria
- Ag limits growth



Fig. 2. FESEM photograph of the silver-deposited HEPA filter with no dust loading (coating time is 60 min).



Yun Haeng Joe, Wei Ju, Jae Hong Park, Young Hun Yoon, and Jungho Hwang. Correlation between the antibacterial ability of silver nanoparticle coated air filters and the dust loading. *Aerosol and Air Quality Research*, 13(3):1009–1018, 2013.

Growth of superstructures

- Nanosecond spark duration
- Mo in air

①Dylec東京ダイレック株式会社

Deposition of MoO₃ on
 Cu foil 3 mm from spark





- Nanoparticles
- Nanoflakes
- Nanowalls
- Nanocrystals
- Nanotubes

 VSpartice
 Figure 3 | SEM images of MoO3 nanostructures. (a-e) Deposited in the pin-to-pin electrode configuration, (f-h) deposited in the pin-to-plate electrode configuration; (i) porous networks of MoO3 deposited in the pin-to-plate configuration.

 David Z. Pai, Kostya (Ken) Ostrikov, Shailesh Kumar, D

David Z. Pai, Kostya (Ken) Ostrikov, Shailesh Kumar, Deanna A. Lacoste, Igor Levchenko, and Christophe O. Laux. Energy efficiency in nanoscale synthesis using nanosecond plasmas. *Scientific Reports*, 3:1221 EP –, Feb 2013. Article.



Synthesis of hollow NPs

- Si around molten Fe
- Fe diffuses inside Si because of temperature gradient



Figure 2. Low- and high-magnification TEM images of individual Si (8.8 ± 2.3) and Fe (26.1 ± 7.9) particles, and their incorporated nanostructures (Si-Fe, 21.8 ± 2.6). Representative SEM images of each sample are also displayed.



Jeong Hoon Byeon and Young-Woo Kim. Ambient plasma synthesis of si-fe hollow nanoparticles and their biocompatibility and lithium storage capacity. *Advanced Materials Interfaces*, 1(5):1300134, 2014.

silicon rod

Increased production rate by increasing the frequency

• Standard operation: 200 Hz (0.3 mg Cu / h) 40

• Large scale:

VSparticle

①Dylec 東京ダイレック株式会社



Fig. 5.2. Decoupling charge and discharge cycles.



T.V. Pfeiffer, J. Feng, and A. Schmidt-Ott. New developments in spark production of nanoparticles. *Advanced Powder Technology*, 25(1):56 – 70, 2014.

Spark behavior in time

- Spark behavior depends:
 - Electrode geometry
 - Electrode gap
 - Gas flow rate

VS**particle**

①Dylec東京ダイレック株式会社



FIG. 5. Images acquired at different delays for spark discharges between tipped-end (upper row) and flat-end (lower row) electrodes placed at 2 mm distance in 10 slm of co-axial N_2 flow. The spark energy was 224 and 427 mJ for the tipped- and flat-end electrodes, respectively. The top electrode was initially the anode in both cases.

J. M. Palomares, A. Kohut, G. Galbács, R. Engeln, and Zs. Geretovszky. A time-resolved imaging and electrical study on a high current atmospheric pressure spark discharge. *Journal of Applied Physics*, 118(23):233305, 2015.
VS**particle**

①Dylec_東京ダイレック株式会社

Patterning by electrostatic focusing



Hoseop Choi, Seunghyon Kang, Wooik Jung, Yoon ho Jung, Sei Jin Park, Dae Seong Kim, and Mansoo Choi. Controlled electrostatic focusing of charged aerosol nanoparticles via an electrified mask. *Journal of Aerosol Science*, 88:90 – 97, 2015.

Particle size distributions from TEM data

- Direct observation of Au particle size 0.4 distributions by TEM
- Comparison of initial size and reference downstream

VS**particle**

①Dylec_東京ダイレック株式会社



Linus Ludvigsson, Bengt O Meuller, and Maria E Messing. Investigations of initial particle stages during spark discharge. *Journal of Physics D: Applied Physics*, 48(31):314012, jul 2015.

Synthesis of single-walled carbon nanotubes

• Growth of SWCNT by Fe NP seeding

VS**particle**

①Dylec_東京ダイレック株式会社





FIG. 4. AFM characterization of SWCNTs synthesized at 880 °C with N $\approx 10^{5} \text{ cm}^{-3}$. The scan window size is $7 \times 7 \,\mu\text{m}^2$. The vertical height profiles of the cross sections 1–6 are shown around the scan window, representing heights between 1 and 1.3 nm (profiles 7–12 can be found in Ref. 14). The histogram shows the statistics of 400 height profiles, with the mean at 1.21 nm.

POIS

FIG. 1. A schema of the synthesis reactor. The spark generator consists of a pair of iron electrodes separated by a discharge gap, continuously flushed by a high-velocity N₂ jet. The discharges evaporate metal from the electrodes, forming catalyst particles that are subsequently fed into the vertical CVD reactor consisting of a quartz tube in a high temperature furnace. A SMPS + E (scanning mobility particle sizer with electrometer) aerosol size classifier consisting of a differential mobility analyser (DMA) and Faraday cup electrometer (FCE) is used to determine the catalyst number concentrations (N) and geometric mean diameter (Dg) prior to introduction into the reactor, and those of the SWCNTs at the reactor outlet.

K. Mustonen, P. Laiho, A. Kaskela, Z. Zhu, O. Reynaud, N. Houbenov, Y. Tian, T. Susi, H. Jiang, A. G. Nasibulin, and E. I. Kauppinen. Gas phase synthesis of non-bundled, small diameter single-walled carbon nanotubes with near-armchair chiralities. *Applied Physics Letters*, 107(1):013106, 2015.

Cluster production at atmospheric pressure

- Measurement of Ag clusters in He gas
- Using generic and purified helium gas
- Selection by DMA
- Detection by uCPC

VSparticle

①Dylec東京ダイレック株式会社



A. Maisser, K. Barmpounis, M. B. Attoui, G. Biskos, and A. Schmidt-Ott. Atomic cluster generation with an atmospheric pressure spark discharge generator. *Aerosol Science and Technology*, 49(10):886–894, 2015.

Increased yield of charged particles

- A bias voltage is maintained
- This repels positive particles
- The yield is doubled

VS**particle**

①Dylec_東京ダイレック株式会社

6000 5000 4000 b voltage (V) 1.2 3000 V2 = 0V2000 1.0 V2 = 3200V V2 = 3400V 1000 V2 = 3600V 0.8 V2 = 3800V0 current (pA) -0.5 0.0 0.5 -1.0 1.0 V2 = 4000Vtime (s) 0.6 6000 0.4 5000 voltage (V) 2000 2000 4000 0.2 0.0 10 30 0 5 15 20 25 1000 particle mobility diameter(nm) 0 -0.5 0.0 -1.0 0.5 1.0 time (s) Seung Ryul Noh, Dae Seong Kim, Sei Jin Park, and Mansoo Choi. En-

hanced yield of positively charged particles from a spark discharge generator via in situ corona discharges. *Journal of Aerosol Science*, 101:188 – 195, 2016.

Deposition of alloy NPs

- Using alloys as starting materials gives alloyed NPs
- The composition is not affected
- The yield can be predicted





Fig. 8 a EDX spectra with the corresponding TEM image using a feedstock with a copper-nickel ration of 40:60, b magnification of the spectra for a better visibility

Alex Muntean, Moritz Wagner, Jörg Meyer, and Martin Seipenbusch. Generation of copper, nickel, and cuni alloy nanoparticles by spark discharge. *Journal of Nanoparticle Research*, 18(8):229, Aug 2016.



Fig. 5 Comparison of the evaporation rate per spark between the Llewellyn Jones model and the measured data

Temperature and quenching rate of the plasma

• Flow rate of 1.68 slpm

VS**particle**

①Dulec東京ダイレック株式会社

- Plasma temperature around 12000 K
- Quenching rate is around 6x10⁸ K/s
- After 25 µs the plasma is at room temperature



Figure 4. The temporal evolution of the intensity of the Cu I 521.82 nm line (open squares) and the evolution of the temperature of the spark plasma derived from the emission spectra (full squares) (2 mm gap, 1.68 slm gas flow rate, 15 mA charging current).

A Kohut, L Ludvigsson, B O Meuller, K Deppert, M E Messing, G Galbács, and Zs Geretovszky. From plasma to nanoparticles: optical and particle emission of a spark discharge generator. *Nanotechnology*, 28(47):475603, oct 2017.

Nanopatterning

VS**particle**

②Dylec東京ダイレック株式会社

- Ion-assisted aerosol litography
- Resist is in a + shape
- Deposition of Cu NPs



Figure 2. SEM images of (a) mono-layer 3D nanostructures and (b) bi-layer 3D nanostructures. The scale bar represents 1 μ m in length.

Kiwoong Lee, Hoseop Choi, Dae Seong Kim, Min Seok Jang, and Mansoo Choi. Vertical stacking of three-dimensional nanostructures via an aerosol lithography for advanced optical applications. *Nanotechnology*, 28(47):475302, oct 2017.

(a)



Figure 3. Numerical calculation results for the particle trajectories and deposition under electric potential distributions formed by accumulated charges on the e-beam resist and assembled nanoparticles. (a) Initial growth stage. (b) Formation of mono-layer 3D nanostructure. (c) Initial growth stage of upper 3D nanostructure after additional e-beam lithography. (d), (e) Lateral growth of upper 3D nanostructure.

Enhanced photocatalysis by plasmonic nanoparticles



• Deposition of Ag, Au, Ag/Au on TiO₂

VSparticle

②Dylec東京ダイレック株式会社

Figure 5. A) IPCE enhancement of TiO_2 films when decorated with 15 nm Ag, Alloy

(Ag/Au) and Au PNPs at 0.2 V vs. SHE. B) Corresponding absorption increase.

Marco Valenti, Anirudh Venugopal, Daniel Tordera, Magnus P. Jonsson, George Biskos, Andreas Schmidt-Ott, and Wilson A. Smith. Hot carrier generation and extraction of plasmonic alloy nanoparticles. *ACS Photonics*, 4(5):1146–1152, 2017.

Scale-up by parallelization

- Example of arc-discharge unit
- Production rate scales linearly







Matthias Stein and Frank Einar Kruis. Scaling-up metal nanoparticle production by transferred arc discharge. Advanced Powder Technology, 29(12):3138 – 3144, 2018.



Influence of electrode diameter



Fig. 8. Influence of copper electrode diameter on particle size and produced mass at standard conditions (left), influence of circuit current on particle size for different copper electrode diameters (middle) and the respective particle size distributions for standard conditions (right).

 Maximilian Domaschke, Melanie Schmidt, and Wolfgang Peukert. A model for the particle mass yield in the aerosol synthesis of ultrafine monometallic nanoparticles by spark ablation. *Journal of Aerosol Science*, 126:133 – 142, 2018. 2078

Core-shell particles

- Carbon encapsulation depends on condensation temperature of C:
 - Tm < Tc: core-shell particle
 - Tm ~ Tc: partially filled particle
 - Tm > Tc: composite





Pelin Livan and Tayfur Ozturk. Carbon encapsulation of elemental nanoparticles by spark discharge. *Journal of Materials Science*, 53(20):14350–14360, Oct 2018.

Production of SERS samples

• Silver nanoparticles



Mohamed Abd El-Aal, Takafumi Seto, Mikio Kumita, Ayman A. Abdelaziz, and Yoshio Otani. Synthesis of silver nanoparticles film by spark discharge deposition for surface-enhanced raman scattering. *Optical Materials*, 83:263 – 271, 2018.



Making alloyed NPs using elemental electrodes

- Ablation produces ions and electrons
- Ions have a stronger albation compared to electrons
- Discharge is oscillatory and can be manipulated

VS**particle**

①Dulec 東京ダイレック株式会社





Figure 5. Mean mixing ratio $\overline{\varphi}_{C}$ as a function of the total resistance R_{tot} used in the spark circuit for $C_{A} = C_{C}$ ($C_{ca} = 45$ nF, $L_{i} = 3 \mu$ H). When R_{tot} increases to a critical damping point ($R_{tot}^{2} = 4L_{i}/C_{ca}$, $R_{tot} \approx 16 \Omega$), only the cathode is ablated due to no polarity reversal.

Figure 1. Schematic illustration of internal NP mixing by using two different electrodes. Variable x indicates the fraction of one (here is material A) electrode material in the resulting NPs, which in turn have a composition distribution. Spatial distribution of vapors produced by the two different electrodes can lead to NPs composed of a single element (i.e., x = 0 or 1).

Jicheng Feng, Nabil Ramlawi, George Biskos, and Andreas Schmidt-Ott. Internally mixed nanoparticles from oscillatory spark ablation between electrodes of different materials. *Aerosol Science and Technology*, 52(5):505– 514, 2018.



Preventing oxidation

	Table 2. C	.01
 Hydrogen is a 		
reducing agent	H ₂ (%)	4
	5	

Table 2. Composition and identified phases of compacted nanoparticles generated in a hydrogen mixture or in nitrogen.

H ₂ (%)	Electrode material	Sinter temperature (°C)	Oxygen (XEDS)		Crystal structure	
			(at%)	(wt%)	XRD	TEM
5	Bismuth	400	34 ± 13	04 ± 1	Bi	Bi
5	Tin	900	34 ± 11	07 ± 3	Sn	Sn
5	Cobalt	700	40 ± 16	15 ± 9	Со	Со
5	Gold	500	27 ± 20	03 ± 2		Au
0	Bismuth	500	60 ± 07	10 ± 3	Bi and Bi ₃ O ₄	Bi and Bi ₃ O ₄
0	Tin	900	72 ± 07	26 ± 7	Low signal*	Sn and/or SnO and SnO ₂
0	Cobalt	700	61 ± 05	30 ± 4	Low signal*	CoO
0	Gold	500	25 ± 10	03 ± 1	_	Au

*The particle concentration was too low for XRD.



R. T. Hallberg, L. Ludvigsson, C. Preger, B. O. Meuller, K. A. Dick and M. E. Messing. Hydrogen-assisted spark discharge generated meta nanoparticles to prevent oxide formation. *Aerosol Science and Technology* 52(3):347–358, 2018.



2070

Self aligning growth of NP-based interconnects



VS**particle** ^①Dylec_東京ダイレック株式会社 S. Leslie, I. Nishchay, N. Helene, R. Johannes Thomas, P. Jörg, and J. Heiko. Self aligning growth of nanoparticle-based interconnects. In 2018 *IEEE 13th Nanotechnology Materials and Devices Conference (NMDC)*, pages 1–4, Oct 2018.

Electrochemical sensor





Fig. 5. CVs of gold redox transitions in 0.1 M H₂SO₄ in dependence on the number of sparks (A) and the values of capacitors in the Cockroft-Walton cascade (C_{int}) and external capacitors (B,C). Anodic dissolution of gold during LSV in 10 mM KBr and 0.1 M HClO₄ at 5 mV/s (D). CVs in 0.1 M H₂SO₄ before and after anodic dissolution experiment (E, CVs have been offset along the y-axis for clarity). The CVs in H₂SO₄ were measured at 100 mV/s; V_{spark} = 1.2 kV; spark cycles: 203 (B), 121 (C); $C_{int} = 2.2 \text{ nF}$ (A). Nyquist plots of eAu/Si-SPEs (F) modified with 43 (scan a) and 203 (scan b) sparking cycles at V_{spark} = 1.2 kV, $C_{int} = 10 \text{ nF}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Maria G. Trachioti, Eleni I. Tzianni, Daniel Riman, Jana Jurmanova, Mamas I. Prodromidis, and Jan Hrbac. Extended coverage of screen-printed graphite electrodes by spark discharge produced gold nanoparticles with a 3d positioning device. assessment of sparking voltage-time characteristics to develop sensors with advanced electrocatalytic properties. *Electrochimica Acta*, 304:292 – 300, 2019. eror.



お問合せ先

Email: info@tokyo-dylec.co.jp Tel: 03-5367-0891(営業部) **Dylec_東京ダイレック株式会社** TOKYO DYLEC CORP.

VSparticle