Electronic Supplementary Materials (ESI) for ChemComm.

Nanostructured silicon ferromagnet collected by a permanent neodymium magnet

Nanostructured Si (N-Si) was prepared by anodic electroetching of a p-type silicon wafer, which was sliced along the (100) plane, in 24% HF-ethanol solution.[1)] The electroetching was carried out under a current density of 100 mA cm^{-2} for 2, 10, 20, or 30 min. The powdered Si was scratched from the wafer with a spatula after the electroetching process, then subsequently rinsed with distilled water and dried in a vacuum oven. The Si wafer, crystalline powder from the Si wafer (C-Si), and the obtained samples, which were labelled as P-Si *x* (*x* = 2, 10, 20, and 30), were used for characterisation by X-ray diffraction (XRD) (UltimaIV, Rigaku), field emission scanning electron microscopy (FE-SEM) (JSM-6330F, JEOL), transmission electron microscopy (TEM) (H-7650, Hitachi), electron spin resonance (ESR) spectroscopy (JES-TE200, JEOL), X-ray photoelectron spectroscopy (XPS) (JPS-9010MX, JEOL), Raman spectroscopy (NRS-3100, JASCO), and SQUID magnetometry (MPMSR2, Quantum Design). XPS spectra were deconvoluted into seven peaks: Si (0), standard; Si (1+) Si_2O, −0.95 eV; Si (2+) SiO, −1.75 eV; Si (3+) Si_2O_3, −2.48 eV; Si (4+) SiO_2, −3.90 eV; Si (4+) thick SiO_2; Si (remaining atom).[2, 3)]

The magnetisation of P-Si *x* depended on the electroetching time (Fig. S1). The Si wafer exhibited a diamagnetic behaviour. Crystalline Si powder obtained from the Si wafer exhibited paramagnetism because of a small and positive magnetisation, which increases linearly with increasing magnetic field.

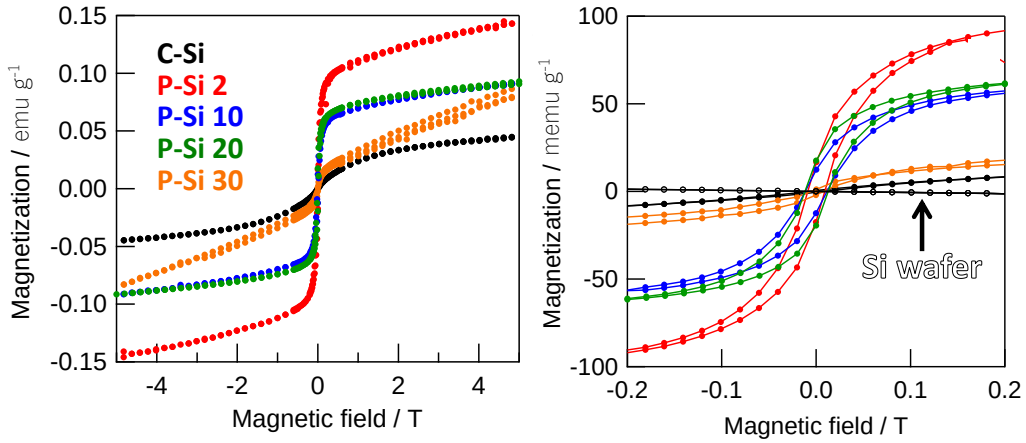

Fig. S1 Magnetisation curves of nanostructured silicon (P-Si *x*) obtained by the electroetching for various times (*x* min), ○: Si wafer; ●: C-Si (crystalline Si powder from Si wafer) at 2 K.

In P-Si *x* samples, a greater saturation magnetisation and coercivity were obtained at shorter electroetching times. The magnet was found to be ferromagnetic because the magnetic hysteresis was observed for all P-Si *x* samples, although the hysteresis loops were very small.

The temperature-dependence curves of a magnetic susceptibility (χ) of the Si wafer, C-Si and P-Si *x* are shown in Fig S2. The Si wafer is diamagnetic, with a negative, small, and constant χ. C-Si is also understood to be paramagnetic because of a positive and higher χ at low temperatures. As shown in Fig. S1, P-Si 2 exhibits the highest χ and is almost insensitive to temperature because it is ferromagnetic and its Curie temperature is greater than 150 K.

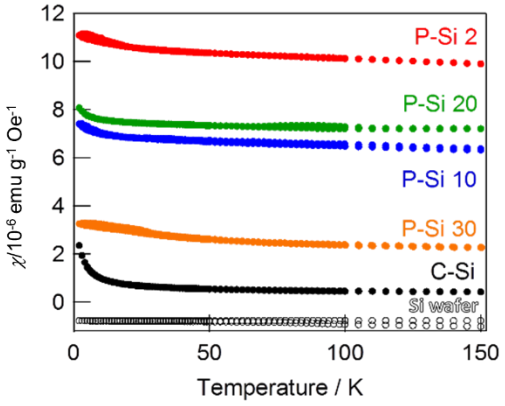

Fig. S2 Temperature dependence of magnetic susceptibility (χ) of nanostructured silicon (P-Si *x*) obtained by the electroetching for various times (*x* min). Magnetic field: 1 T.

Fig. S3 shows the XRD patterns of the C-Si and P-Si *x* samples. The pattern of C-Si is a typical pattern of powdered Si. The patterns of P-Si 20 and 30 are similar to that of C-Si, although the peaks are broad because of the low crystallinity of the P-Si *x* samples. By contrast, the patterns of P-Si 2 and 10 differ slightly, showing a relatively strong peak assigned to the (400) plane. The intensity of this peak is attributed to the Si wafer being sliced along the (100) plane. The P-Si 2 and 10 samples had a residual structure oriented to the plane of the Si wafer because of the short electroetching time. The primary particle size was calculated from the patterns using the Scherrer equation: > 100 nm, 43 nm, 34 nm, 29 nm and 17 nm for C-Si, P-Si 2, P-Si 10, P-Si 20 and P-Si 30, respectively. Thus, the P-Si *x* samples are nanostructured solids.

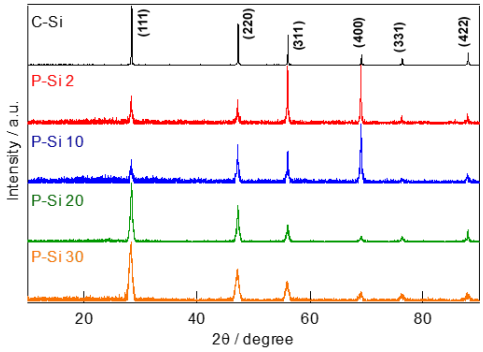

Fig. S3 XRD patterns of nanostructured silicon (P-Si *x*). X ray target: Cu Kα

The porosity of P-Si *x* samples was examined via N_2 gas adsorption measurements at 77 K; the results are shown in Fig. S4. The C-Si is found to be

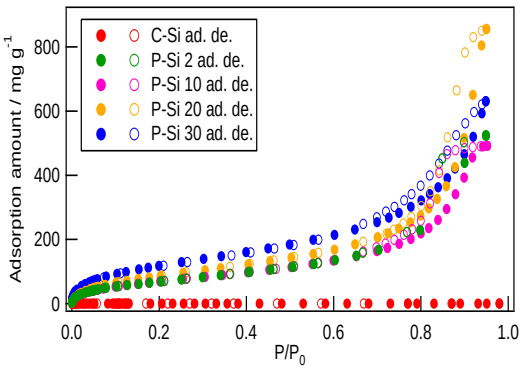

Fig. S4 N_2 adsorption isotherms of P-Si *x*. Closed: adsorption; open: desorption

nonporous, whereas P-Si *x* samples are mesoporous. The pore size distribution was obtained via Barrett–Joyner–Halenda (BJH) analysis of the isotherms (Fig. S5). All of the P-Si *x* samples have mesopores with pore diameters 10 nm or larger. The longer etching times caused a broad pore size distribution for pores larger than 15 nm. Thus, the electroetching produced nanopores on the Si crystal. The nanostructure should be intrinsic to the ferromagnetism of P-Si *x*.

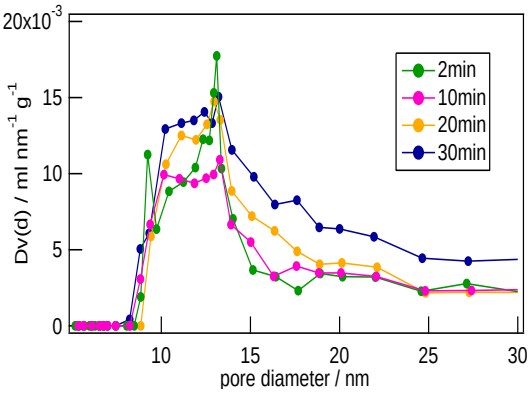

Fig. S5 Pore size distribution after the BJH analysis from the N_2 adsorption isotherms of P-Si *x* (Fig. S4).

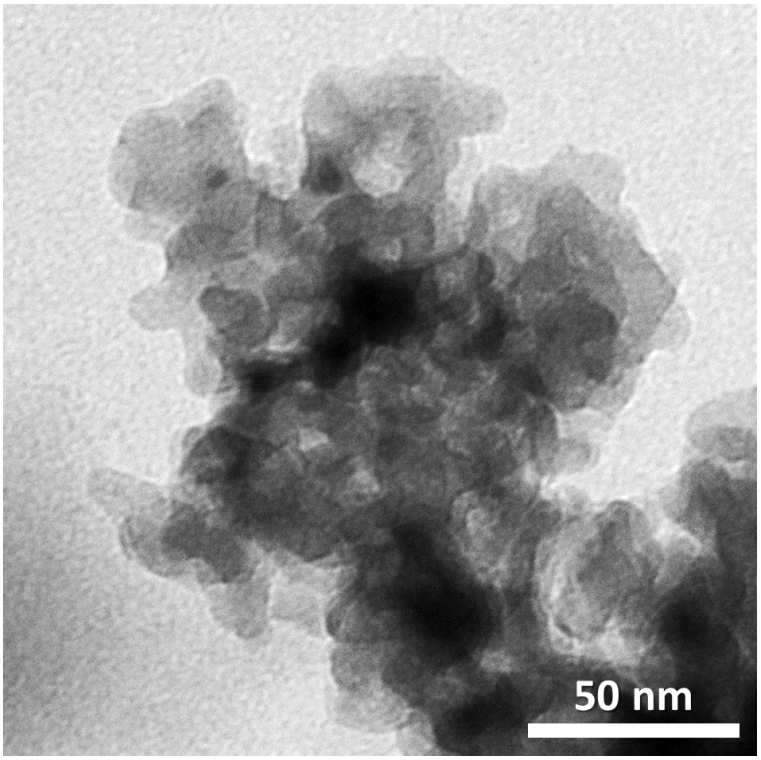

Fig. S6 TEM image of mN-Si.

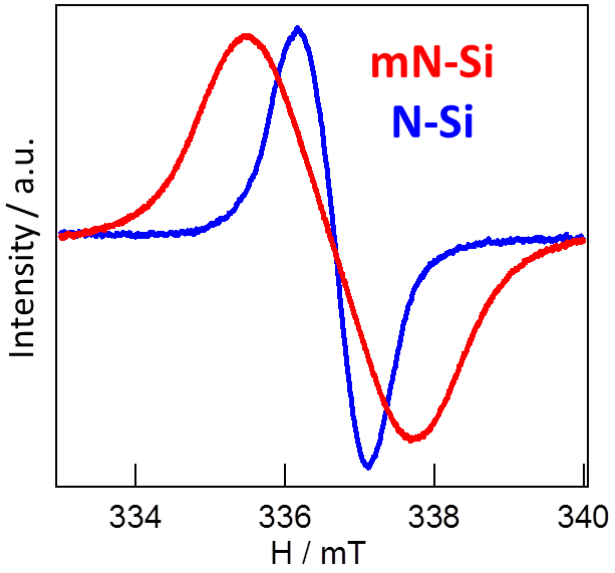

Fig. S7 Electron spin resonance (ESR) spectra of N-Si (blue) and mN-Si (red).

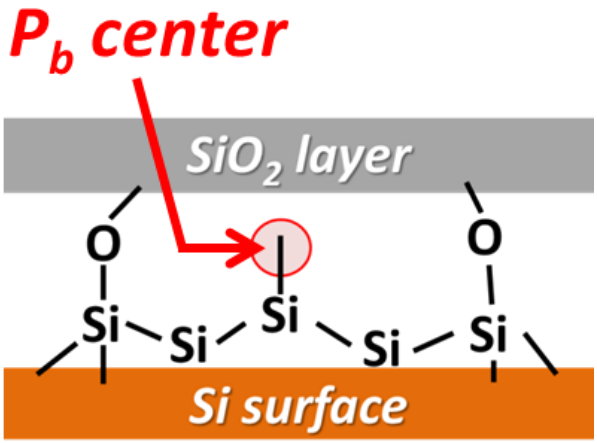

Fig. S8 Electron spin formed in a silicon nanostructure.[4)]

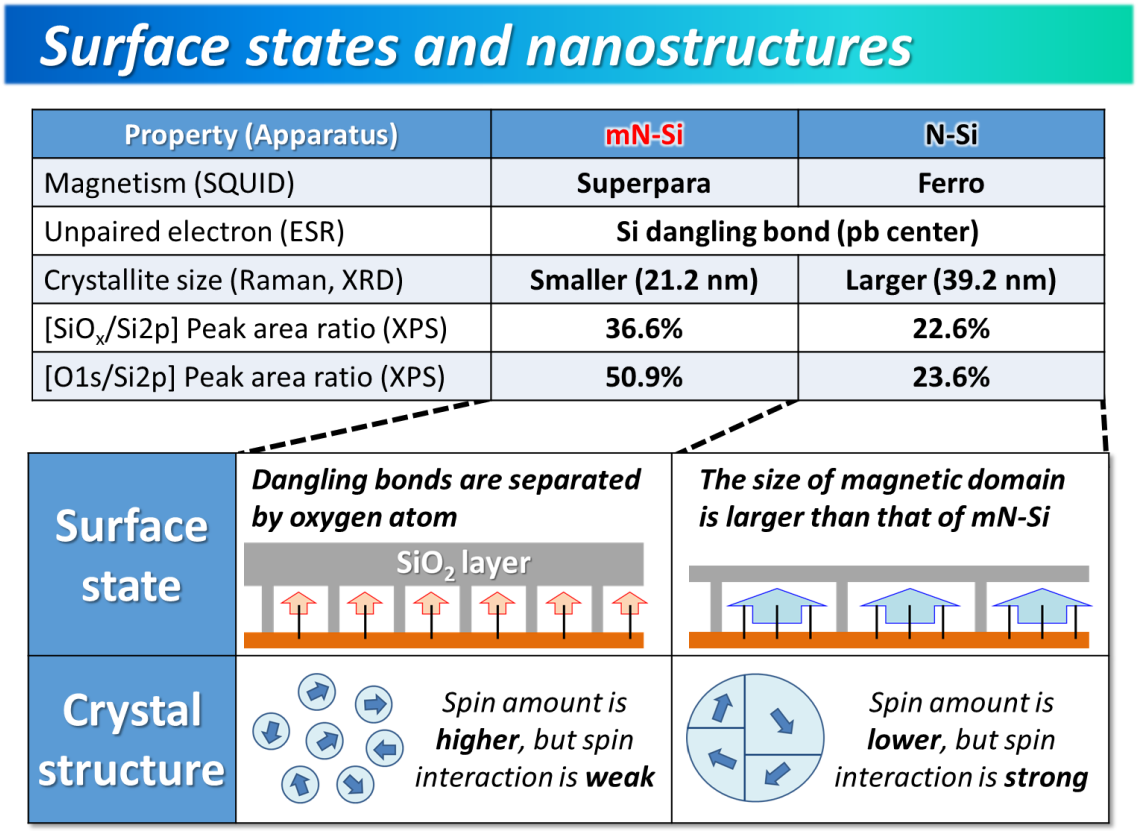

Fig. S9 Surface states and nanostructures of N-Si and mN-Si.

References

1) V. Lehmann and H. Föll, *J. Electrochem. Soc.,* **1990**, 137, 653–659.
2) F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi and J. A. Yarmoff, *Phys. Rev. B*, **1988**, 38, 6084–6096.
3) Th. Eickhoff, V. Medicherla and W. Drube, *J. Electron Spectrosc. Relat. Phenom*., **2004**, 137–140, 85–88.
4) Y. Uchida, N. Koshida, H. Koyama and Y. Yamamoto, *Appl. Phys. Lett.*, **1993**, 63, 961–963.