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REGULAR PAPER

Formation of nanocrystalline silicon in SiO$_x$ by soft X-ray irradiation at low temperature

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The low-temperature formation of nanocrystalline Si (nc-Si) in SiO$_x$ film is one of the key technologies in the realization of Si-based photonics and memories. We proposed a low-temperature nc-Si formation method with soft X-ray irradiation. The nc-Si formation depended on the Si/O atomic ratio in the pristine SiO$_x$ film. The Si-rich regions in SiO$_x$ films with Si/O ratios higher than 0.67 were crystallized by atomic migration via electron excitation with soft X-ray irradiation at a photon energy near the core level of Si 2p. nc-Si with a mean size of 20 nm was formed by soft X-ray irradiation at a low temperature of 660 °C. © 2017 The Japan Society of Applied Physics

1. Introduction

The nanocrystalline Si (nc-Si) in SiO$_x$ films is one of the attractive materials for use in Si-based photonics and memories.[1–3] Complementary metal–oxide–semiconductor (CMOS) technology with photonics is expected for next-generation Si technology.[4] In addition, the nc-Si in SiO$_x$ films is one of the key technologies in the realization of high-quality solar cells with quantum cutting.[5] The nc-Si in SiO$_x$ films is obtained by various methods,[6–9] in which the SiO$_x$ single layer[10] and Si/SiO$_2$ superlattice[11] are used as starting materials. In general, furnace annealing (FA) is used to form nc-Si. In FA, a high annealing temperature above 1000 °C is necessary for the formation of nc-Si.[12,13] This annealing temperature is too high to apply the CMOS process.

The authors have developed a novel semiconductor fabrication process using high-brightness soft X-rays.[14–21] The effects of electron excitation and atomic migration upon soft X-ray irradiation from a 2.28 m undulator at the synchrotron radiation facility NewSUBARU[22] and a laser plasma X-ray (LPX) source on the crystallization of amorphous semiconductor films were investigated. The LPX system is compact in size compared with the synchrotron radiation facility and is expected to be used in industry.[23,24] It was clarified that the critical temperatures for the crystallization of a-Si, a-Ge, and a-SiGe films are reduced by approximately 100 °C in comparison with conventional FA. In addition, the low-temperature activation of boron in a Si wafer is realized by using this technique.[21] Therefore, it is expected that nc-Si can be obtained by soft X-ray irradiation at a low temperature. In this study, we intended to form nc-Si in SiO$_x$ films by soft X-ray irradiation.

2. Experimental procedure

SiO$_x$ films with various Si/O ratios were deposited on a quartz substrate ($18 \times 20 \times 0.5$ mm^3) by reactive sputtering. The distance between the substrate and the target was 100 mm. The sputtering rf power was 300 W. The pressure in the chamber was 1.33×10^{-1} Pa during film deposition. The sample holder was cooled by water and the sample holder temperature was kept at 24 °C. The thickness of SiO$_x$ films was 50 or 300 nm. To vary the Si/O ratio of SiO$_x$ films, the Ar/O$_2$ gas flow ratio was changed from 8.3/1.7 to 9.4/0.6. The total flow rate of the mixture of O$_2$ and Ar gases was 10 sccm. Under these conditions, the Si/O ratio was varied from 0.5 to 1.23. These Si/O ratios of the SiO$_x$ films were measured by X-ray photoelectron spectroscopy.

Soft X-ray irradiation was carried out at BL07A in the synchrotron radiation facility NewSUBARU. The soft X-ray irradiation apparatus is schematically illustrated in Fig. 1. The storage-ring energy and storage-ring current were 1.0 GeV and 300 mA, respectively. The irradiated photon energy of the 3rd-order light was 115 eV. This photon energy relates to the core level of Si 2p. In this experiment, a monochromator was not used for selecting the irradiating photon energy. Therefore, much higher-order light was included in the irradiated soft X-rays. From the photon flux calculation, the photon energies of the 1st-, 3rd-, 5th-, and 7th-order light were 38, 115, 192, and 268 eV, respectively. The photon flux ratios of the 1st-, 5th-, and 7th-order light to the 3rd-order light were 1.1, 0.52, and 0.30, respectively. In this apparatus, photons below 50 eV were cut by a filter. Therefore, the 3rd-order light of 115 eV mainly irradiated the sample under this condition. The absorptions of Si and SiO$_2$ of 50 nm thickness were estimated to be 0.63 and 0.52, respectively.[25] The dose was fixed at 50 mA·h. In this case, the irradiation time was 600 s. The soft X-ray beam size on the sample surface was 7.5 mmϕ. The sample temperature during soft X-ray irradiation was monitored with a pyrometer using an emissivity of 0.8.[15] The sample temperature was automatically increased by radiant energy during soft X-ray irradiation in spite of not using a heater. The sample temperature was saturated at 660 °C for 120 s.

To clarify the difference between the mechanisms of nc-Si formation with soft X-ray irradiation and with FA, 300-nm-thick SiO$_x$ films were also prepared on a quartz substrate by reactive sputtering under the above-mentioned conditions. These samples were annealed at 1000 and 1050 °C for 3600 s in an infrared furnace as a reference. Unfortunately, these SiO$_x$ films were not the same as the soft-X-ray-irradiated samples. As mentioned later, it is considered that the difference between soft X-ray irradiation and FA can be discussed in spite of the samples having different Si/O ratios and film thicknesses.

The structural properties of the nc-Si in SiO$_x$ films were evaluated by Raman scattering spectroscopy. The crystalline

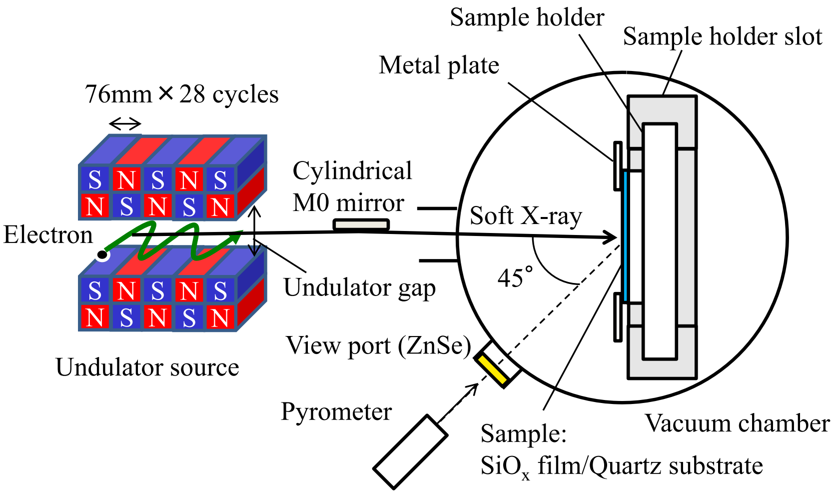

Fig. 1. (Color online) Schematic diagram of soft X-ray crystallization apparatus. Soft X-ray is generated from a 2.28 m undulator at BL07A in the synchrotron facility, NewSUBARU. The sample temperature during soft X-ray irradiation was monitored with a pyrometer. The sample temperature during soft X-ray irradiation was 660 °C.

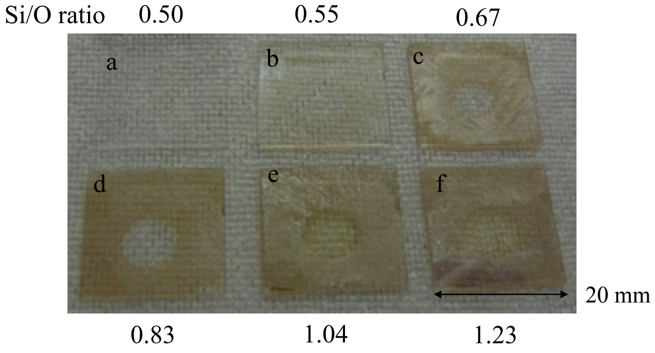

Fig. 2. (Color online) Optical image of the samples with Si/O ratios between 0.5 and 1.23 after soft X-ray irradiation. The ratios of Ar : O flow rates of samples a, b, c, d, e, and f were 8.3 : 1.7, 9.0 : 1.0, 9.1 : 0.9, 9.2 : 0.8, 9.3 : 0.7, and 9.4 : 0.6, respectively. The sample color changed in the center circle, which corresponds to the irradiation region.

fraction of the Si phases in SiO$_x$ films was estimated using the ratio of the crystal phase to the sum of amorphous (480 cm^{-1}) and crystal (521 cm^{-1}) phases.[26,27] The peak position and full width at half maximum (FWHM) of the Raman peak are related to the film stress, defect density, and grain size.[28,29] The mean size of nc-Si (L_0) was estimated from $\Delta\omega$ in Raman spectra as

$$\Delta\omega = \frac{A}{L_0^x}, \tag{1}$$

where $\Delta\omega$, A, and x are the shift from the Raman peak of single-crystal Si (521 cm^{-1}), $154 - 10^{-2}\sigma^{-2.22}$, and $1.59 - 1.08 \times 10^{-3}\sigma^{-2.15}$, respectively.[30] σ is the size dispersion parameter. In this study, L_0 was estimated by assuming $\sigma = 0$.

3. Results and discussion

An optical image of the samples after soft X-ray irradiation is shown in Fig. 2. The color in the irradiation regions of all the samples changed after soft X-ray irradiation. The color change was caused by the transition from amorphous to crystalline phases.[18] As mentioned later, it is considered that amorphous Si (a-Si) phases were crystallized by atomic migration via electron excitation by soft X-ray irradiation at the photon energy near the core level of Si 2p.

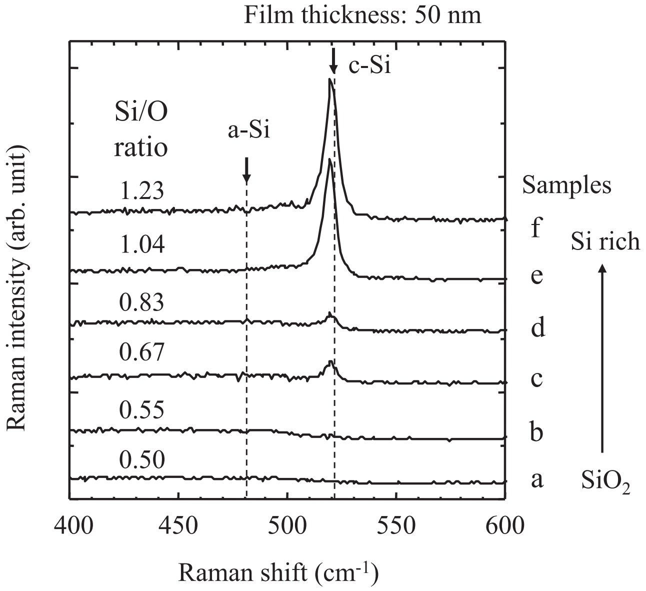

Fig. 3. Raman spectra of SiO$_x$ films after soft X-ray irradiation. The Raman spectra were obtained at the center of the soft-X-ray-irradiated region. The dotted lines show the Raman peak positions of crystal and amorphous Si phases.

The Raman spectra of the soft-X-ray-irradiated region in the SiO$_x$ films are shown in Fig. 3. Only a broad peak at around 480 cm^{-1}, corresponding to a-Si phases, was observed outside of the soft-X-ray-irradiated region (nonirradiated region) of the sample with the Si/O ratio of 1.23. On the other hand, a sharp peak near 521 cm^{-1}, corresponding to c-Si phases, was also observed in the irradiation region of the same sample. Similar peaks at 480 and 521 cm^{-1} were observed in the samples with Si/O ratios above 0.67, indicating that a-Si phases in SiO$_x$ films were crystallized. In addition, the Raman intensity increased with increasing Si/O ratio, indicating that the density of nc-Si increased with increasing Si/O ratio. For Si/O ratios of 0.5 and 0.55, the peak due to the crystal phase was not observed. It is found

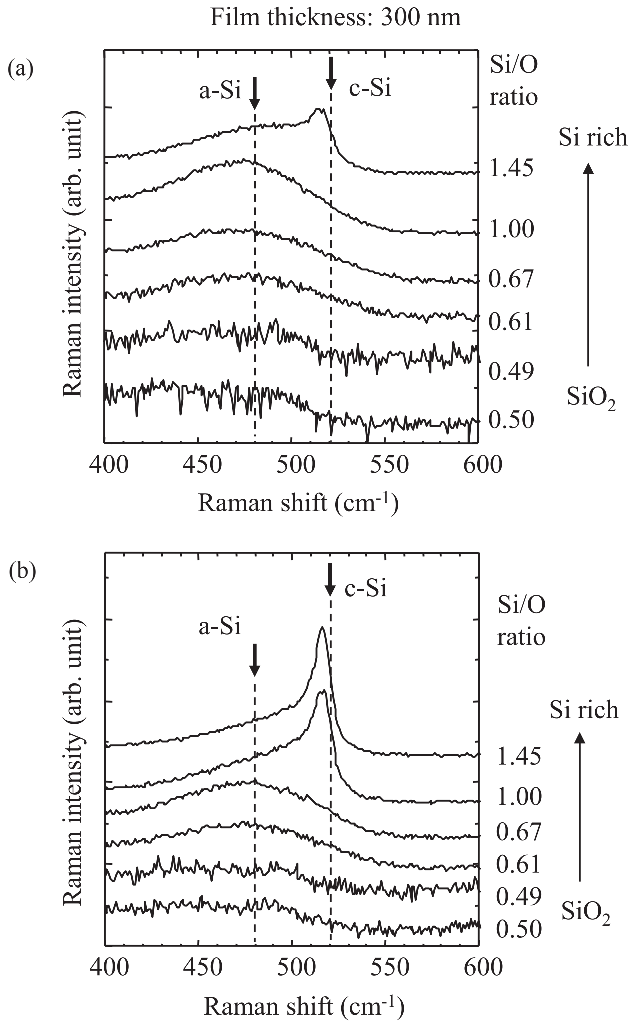

Fig. 4. Raman spectra of the SiO$_x$ films after FA at 1000 (a) and 1050 °C (b). The dotted lines show the Raman peak positions of crystal and amorphous Si phases.

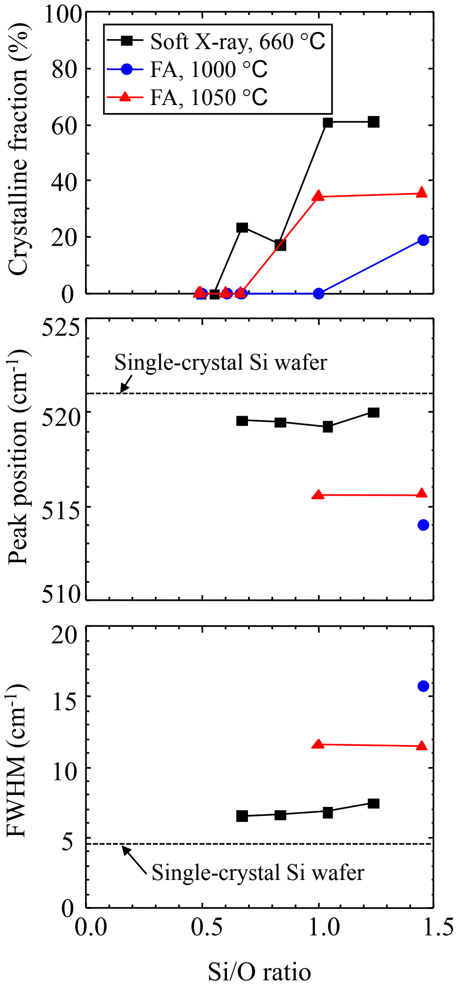

Fig. 5. (Color online) Peak position, FWHM, and crystalline fraction as functions of the Si/O ratio. The peak position and FWHM of single-crystal Si are also indicated by the dotted line.

that the crystallization of a-Si phases in SiO$_x$ films upon soft X-ray irradiation is related to the excess Si fraction.

The Raman spectra of SiO$_x$ films treated by FA at 1000 and 1050 °C are shown in Figs. 4(a) and 4(b), respectively. Only the SiO$_x$ film with the Si/O ratio of 1.45 was crystallized by FA at 1000 °C. As the annealing temperature was increased from 1000 to 1050 °C, the SiO$_x$ film with the Si/O ratio of 1.00 was also crystallized. In the crystallization of the a-Si film by FA, the a-Si phases become the polycrystalline phases completely at a high annealing temperature of 1000 °C. On the other hand, the a-Si phases in SiO$_x$ were not easy to crystallize because the atomic movement of Si was suppressed by strong Si–O bonds.

The peak position, FWHM, and crystalline fraction estimated from Raman spectra as functions of the Si/O ratio are shown in Fig. 5. In the soft X-ray irradiation, the crystalline fraction at the center of the soft-X-ray-irradiated region increased from 0 to 60% with increasing Si/O ratio. Although the sample temperature in soft X-ray irradiation was lower than the annealing temperature in FA, the crystalline fraction after soft X-ray irradiation was higher than that after FA. The low-Si/O-ratio SiO$_x$ films were difficult to crystallize by either soft X-ray irradiation or FA. It is considered that the cohesion of Si atoms did not occur because the distance between the nearest-neighbor Si atoms was large for the low-Si-fraction films. As the Si/O ratio is increased, the cohesion of Si atom is enhanced. Therefore, the crystal phase (crystalline fraction) was increased by increasing the Si/O ratio. With soft X-ray irradiation, the a-Si film is crystallized at a low temperature of 580 °C[15] because the diffusion coefficient of Si atoms in Si is larger than that in SiO$_2$.[31,32] Therefore, a high sample temperature is necessary for the formation of nc-Si in SiO$_x$. During soft X-ray irradiation, the atomic migration is enhanced by electron excitation. Therefore, it is considered that the low-temperature formation of nc-Si was realized. The Raman peak position and FWHM of SiO$_x$ films with various Si/O ratios were almost constant in the case of the soft X-ray irradiation. The Raman peak positions of the SiO$_x$ films crystallized by FA were lower than those in the case of soft X-ray irradiation. It is known that FWHM is increased by decreasing the size of nc-Si.[30] In addition, FWHM was influenced by the grain size distribution and defect density in crystal grain. On the other hand, the FWHM of FA samples was large. The mean size of the nc-Si in SiO$_x$ films is shown in Fig. 6. These sizes of nc-Si were estimated from the peak position using Eq. (1). In the soft-X-ray-irradiated samples, the sizes of nc-Si were estimated to be 16–23 nm. In the FA sample with the Si/O ratio of 1.00, as the annealing temperature was increased from 1000 to

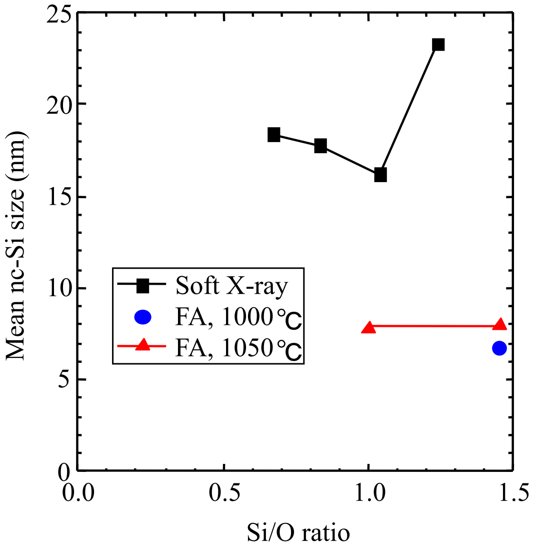

Fig. 6. (Color online) Mean size of nc-Si in SiO$_x$ film prepared by soft X-ray irradiation and FA at 1000 and 1050 °C, respectively. The thicknesses of SiO$_x$ films subjected to soft X-ray irradiation and FA were 50 and 300 nm, respectively.

1050 °C, the mean size of nc-Si slightly increased from 6.7 to 7.9 nm. It is considered that the growth of nc-Si in SiO$_x$ was enhanced by thermal energy. When the mean size of nc-Si is similar to the thickness of the SiO$_x$ film, it appears that the mean size of nc-Si in the SiO$_x$ film depends on the thickness of the SiO$_x$ film. However, the mean size of nc-Si prepared by both methods was smaller than the SiO$_x$ film thickness. Although the thicknesses of SiO$_x$ films subjected to the soft X-ray irradiation and FA treatment are different, it is considered that the difference between the soft X-ray irradiation and the FA can be discussed. It is reported that the size of nc-Si is increased by increasing the treatment time.[12] Therefore, it is speculated that a small nc-Si can be obtained with a short duration of soft X-ray irradiation.

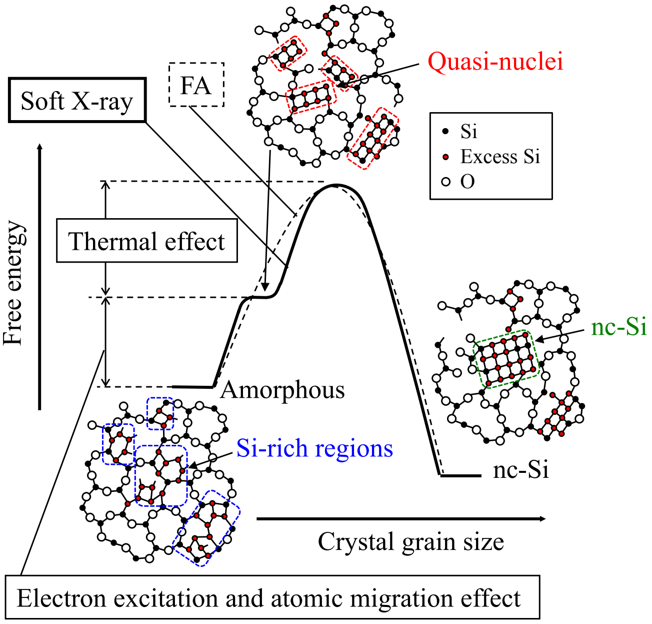

Fig. 7. (Color online) Schematic diagram of the formation mechanism of nc-Si upon soft X-ray irradiation. Quasi-nuclei were formed by irradiation in the Si-rich region. The critical energy density (activation energy) for nc-Si formation (crystallization) was decreased by soft X-ray irradiation.

Next, we discuss the advantages and mechanism of nc-Si formation under soft X-ray irradiation (Fig. 7). The crystallization mechanism of a-Si irradiated with soft X-rays is explained as follows.[15,20] During soft X-ray irradiation, the electrons in the Si core levels are excited to the vacuum level and the ionization of Si atoms occurs. In this case, the atomic movement of Si is enhanced by the composition of local lattice vibrations and Coulomb force between Si atoms. Consequently, the atoms are locally reordered. This implies that the crystal-like region is formed via the local movement of atoms. We call this region the quasi-nucleus. The quasi-nuclei grow to the critical radius of crystallization owing to thermal effects. In this case, these crystal grains can be grown without the need for nucleation energy to be supplied in the crystallization process, because the quasi-nuclei are already formed. The critical crystallization temperature decreases because of the presence of the quasi-nuclei that formed as a result of the soft X-ray irradiation. In the case of nc-Si formation in the SiO$_x$ film, the Si atoms in the SiO$_x$ film are difficult to move because the Si–O bond is strong and stable. The energy of the irradiated soft X-ray was 115 eV, which is higher than the binding energies of Si–Si (3.37 eV) and Si–O (8.30 eV).[33] Therefore, the soft X-ray breaks Si–Si and Si–O bonds. This bond breaking can enhance reconstruction, and the Si atoms can begin to move at a sample temperature lower than the annealing temperature in FA. Therefore, the critical temperature for nc-Si formation was decreased by 340–390 °C in comparison with FA. It is considered that the low-temperature formation is one of the advantages of applying soft X-ray irradiation to MOS fabrication processes.

4. Conclusions

A novel formation method for the nc-Si in SiO$_x$ film was proposed and the formation mechanism was investigated. The following results were obtained. 1) The a-Si phases (Si-rich region) in SiO$_x$ films crystallized upon soft X-ray irradiation, and the mean size of nc-Si was estimated to be about 20 nm from the Raman peak position. 2) Although the sample temperature for soft X-ray irradiation was lower, 340–390 °C, than the annealing temperature for FA, the mean nc-Si size after soft X-ray irradiation was larger than that after FA. 3) It is considered that a-Si (Si-rich region) in SiO$_x$ films was crystallized by atomic migration as a result of electron excitation by soft X-ray irradiation at a photon energy near the core level of Si 2p. The soft X-ray breaks Si–Si and Si–O bonds. Therefore, nc-Si was formed by soft X-ray irradiation in spite of the low temperature of 660 °C. 4) It is expected that this novel nc-Si formation technique of using high-brightness soft X-rays will be applied in the CMOS fabrication process, enabling Si-based photonics and memories to be realized.

Acknowledgments

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