Enhancing silicide formation in Ni/Si(111) by Ag-Si particles at the interface

Cheng-Hsun-Tony Chang1,2,3, Pei-Cheng Jiang4,2, Yu-Ting Chow1, Hsi-Lien Hsiao4, Wei-Bin Su2 & Jyh-Shen Tsay1

Compound formation at a metal/semiconductor interface plays crucial roles in the properties of many material systems. Applications of Ni silicides span numerous areas and have the potential to be used as new functionalities. However, the magnetic properties of ultrathin Ni layers on silicon surfaces and related chemical compositions at the interface are not fully understood and the influence of Ag additives on the reactivity of Ni/Si(111) remain unclear. We report herein on the fact that the dominant species produced at the interface is NiSi, which is produced by the spontaneous formation of strong bonds between Ni and Si atoms. Assuming that a Ni layer is formed over a NiSi layer with the total coverage as a constraint, we established a chemical shift-related concentration model that, in effect, represents a practical method for determining the amount of ultrathin Ni silicides that are produced at the buried interface. The formation of Ag-Si particles provide a viable strategy for enhancing silicide formation via a specific interaction transfer mechanism, even at room temperature. The mechanism is related to differences in the enthalpies of formation \( \Delta H_{\text{Ag-Si}} \), \( \Delta H_{\text{Ni-Ag}} \) and \( \Delta H_{\text{Ni-Si}} \) for these phases and provides insights into strategies for producing ultrathin silicides at a buried interface.

Metal-semiconductor interfaces have attracted considerable interest because of their promising applications as semiconductor devices and possible use as new functionalities in semiconductor technology1–5. Owing to the high chemical reactivity of semiconductor surfaces, the formation of compounds at metal/semiconductor interfaces plays crucial roles in determining the properties of material systems and open a wide range of applications6–17. For example, cobalt di-silicide shows intrinsically low noise properties which could be utilized for developing superconducting circuits and qubits in the future quantum computing6. Metal silicides have been shown to have the ability of catalyze various reactions, especially hydrogenation, due to their specific crystal and electronic structures10. For higher conversion efficiencies of the optical absorption spectrum, \( \beta \)-FeSi2-containing SiO2 composites provide desirable selective absorbing behavior9. Moreover, the formation of compounds at metal/semiconductor interfaces are induced by impurities16–19. At elevated temperatures, the interaction transferring for Si atoms through a \( (\sqrt{3} \times \sqrt{3})R30^\circ \text{Ag} \) layer causes a gradual interaction between Si and Co and the resulting smooth surface is advantageous in terms of stabilizing the easy axis of magnetization16. The distribution of substitution alloying elements in the \( \gamma \)-Nb5Si3, which serves as a reinforcing phase of the composite based on Nb–Si18. By implanting nitrogen under the critical conditions, the growth of metal-rich silicide phases is circumvented, as the Ni film converts to the amorphous NiSi phase during annealing19. Because of the interest in developing novel spintronic devices, explorations directed toward attempting to combine the charge and spin degrees of freedoms have increased dramatically12–28. Based on a successful combination of a solution process and the efficient control of the electric potential for magnetism, a novel concept of electric-potential-tuned magnetic recording has been developed, resulting in the development of stable recording media with a high degree of writing ability20. The formation of CoSi2 compounds at the interface on a Si(111) surface occurs and the easy axis of magnetization of Co/Si films is canted out-of-plane due to interfacial effects14. By tuning the contact areas of Ag and Ni at the Ag/Ni interface, it is possible to change the coercive force of the films by modifying the magnetic anisotropy energy15. By controlling interface band alignment, the functionality of the EuO/Si spin contact shows a conduction band offset of 1.0 eV, a value that is competitive with charge electronics24.
Nickel is widely used as a catalyst, including for fabricating various nanostructures, and in water splitting, hydrogen production, and sulfurization processes. Nickel is also widely used in steel alloys and electroplating. As a magnetic material, nickel has an advantage of a relatively low Curie temperature (627 K), which permits it to be used in studies of critical phenomena near room temperature. The relatively small coercive force of nickel allows Ni-based thin films to be studied under relatively low external fields. Silicon is the most important substrate that is used in fabricating microelectronic components. Because of the low resistivity and low fabrication temperature, Ni/Si systems are widely used in the electronics industry as ohmic contacts and interconnects. Applications of Ni silicides span numerous areas, including their use in silicon complementary metal–oxide–semiconductors, field effect transistors, batteries, and floating gate memory. Ni, Si, NiSi, and NiSi₂ all appear to be present at Ni/Si interfaces and the composition is dependent on the temperature of the sample and the preparation procedure. There are relatively few reports dealing with the magnetic properties of ultrathin Ni layers on silicon surfaces and chemical compositions of these materials at the interface. In additional, the influence of Ag additives on the reactivity of Ni/Si(111) remain unclear. In this study, we report on an investigation of the morphologies, chemical states and related magnetic properties of Ni/Si(111). NiSi is the relatively dominant species found at the Ni/Si interface because of the strong bonding between Ni and Si atoms. Assuming that a Ni layer is formed over a NiSi layer with the total coverage as a constraint, we established a chemical shift-related concentration (CSRC) model that represents a practical method for determining the amount of ultrathin Ni silicides that are produced at the buried interface. For a submonolayer Ni deposited on a few monolayers of Ag/Si(111), the chemical state of Ni was found to be closer to that for Ni silicides rather than for Ni-Ag bonding. This is the first observation to confirm that Ag-Si particles serve as a catalyst to promote the chemical interaction of Ni and Si to form Ni silicides. The mechanism is related to the differences in the enthalpies of formation ΔH_{Ag-Si}, ΔH_{Ni-Ag}, and ΔH_{Ni-Si}, and provide insights into strategies for producing ultrathin silicides at a buried interface.

Results and Discussion

All experiments were conducted in an ultrahigh vacuum (UHV) chamber to avoid possible contamination from the residual gases. The Si(111) surface was cleaned by Ar⁺ ion bombardment and annealed at 1250 K. The sputtering-annealing cycles followed by slowly cooling to room temperature were continued until a well-ordered 7 × 7 structure could be obtained by low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) techniques. The cleanliness of the specimen was checked by Auger electron spectroscopy (AES). Ni atoms were evaporated by passing an electronic current through a resistively heated Ni coil. The detailed information about the sample preparations are described in the method section as well as in our previous reports.

During the deposition of Ni on Si(111)-7 × 7, the morphological evolution of Ni/Si interfaces was investigated using an STM technique. STM images for 0.8, 2.4, and 5 monolayer (ML) Ni/Si(111) are shown in Fig. 1a-c, respectively. For imaging the silicide related defects on the Si(111)-7 × 7 substrate, a negative bias potential (V_{bias}) at −1.5 V was used. As shown in Fig. 1a for 0.8 ML Ni/Si(111), dark defects can be seen on the rhombic unit cell of the Si(111)-7 × 7 substrate. The dark defects are similar to that in Co/Si(111) for which the presence of Co silicides have been reported. For 0.8 ML Ni/Si(111), the dark defects are related to the formation of Ni silicides. The dark defects have different sizes, which can be attributed to different chemical states of Ni silicides. For the case of 2.4 ML Ni/Si(111) in Fig. 1b, small clusters with oval shapes can be seen. This is due to the accumulation of Ni atoms to form clusters. For the case of the thicker Ni/Si(111) in Fig. 1c (5 ML), the surface morphology is rather smooth indicating the formation of a continuous film. These structural findings are important for the further analysis of magnetic properties of Ni/Si(111) ultrathin films.

Using the surface magneto-optic Kerr effect (SMOKE) technique at room temperature, Kerr signals versus the magnetic field in both the longitudinal and polar configurations are shown in Fig. 1d. At the initial stage of the Ni deposition (3 ML), no hysteresis is detectable in either of the configurations, but hysteresis clearly occurs at thicker Ni/Si(111) (6 ML). As the Ni coverage increases (9 ML), both the saturated Kerr intensities and coercive forces become larger. The coercive force in the case of the polar configuration is ten times larger than that in the longitudinal configuration. This result shows that the preferred easy axis of magnetization for Ni/Si(111) lies on the surface plane. Since the in-plane component dominates the magnetic anisotropy, in the following discussion, we focus on the magnetic properties only in the longitudinal configuration. Figure 1e shows the saturated Kerr intensity and coercive force versus Ni coverage in the longitudinal configuration. At the initial stage of Ni deposition, the Kerr intensity is zero for the first 4 ML while the Kerr intensity is nonzero at a thickness of around 5 ML. For Ni/Si(111) thicker than 5 ML, the Kerr intensity increases linearly with increasing Ni coverage. This shows that ferromagnetic films were formed with a Curie temperature well above room temperature. For Ni/Si(111) with a coverage between 1.8 and 5 ML, the zero value of the Kerr intensity can be attributed to the finite size effect resulting from the formation of Ni clusters. The thermal agitation of the magnetization diminishes the exchange coupling between atomic magnetic moments in Ni clusters. Therefore, Ni/Si(111) adopts a phase comprised of paramagnetic clusters. On the other hand, the coercive force increases rapidly from 7.5 to 30 Oe for 5 to 7 ML Ni and reaches a steady value of 30 Oe for thicknesses of up to 11 ML. This is due to the effects of reduced dimensionality, reflecting the evolution of the magnetic anisotropy energy for thin films. The results of SMOKE measurements with three phases in different coverage regimes for ultrathin Ni/Si(111) films are shown at the bottom of Fig. 1e and include (I) nonmagnetic silicides, (II) clusters with lowered Curie temperatures, and (III) ferromagnetic films.

To obtain further information related to silicide formation for Ni adatoms on Si(111)-7 × 7, the morphological evolution of Ni/Si interfaces were explored using the STM technique. As an example, Fig. 2a shows an STM
image for 0.02 ML Ni/Si(111) at a negative $V_{bias}$. Different sized dark defects are clearly observed on the surface. This phenomenon is different from the Co silicide formation process for Co deposition on Si(111)-7×7, where only double-dark spots are detected, indicating that the dominant species in this case is CoSi$_2$. The appearance of different sized, dark defects for Ni deposited on Si(111)-7×7 suggests that different species of Ni silicides are produced. At the initial stage of Ni deposition on Si(111)-7×7, the number of defects increases with increasing...
Ni coverage. In order to carry out a quantitative analysis, the defects were categorized according to the number of dark spots in a unit cell, B1, B2, and B3, as shown in Fig. 2b–d, respectively. The areal densities for B1, B2, and B3 are defined as the ratios of B1, B2, and B3 unit cells per total unit cells, respectively. The statistics for the areal densities of B1, B2, and B3 are shown in Fig. 2e, calculated from STM images of 50 × 50 nm² areas for small amounts of Ni atoms on Si(111). By increasing the coverage of Ni, the areal densities of B1, B2 and B3 increase while the slopes for these increases are different. After examining the STM images, single-dark spots (B1) occur randomly on the Si(111) surface. Ni adatoms have no particularly preferred site for their bonding on the rhombic unit cells of the Si(111)-7×7 substrate. The B1 spot is related to the formation of NiSi and can be attributed to the presence of strong bonding between Ni and Si atoms. In addition, the areal density of B1 is much larger than those for B2 and B3. This shows that NiSi is the relatively dominant species at the Ni/Si interface during the deposition of Ni. Because of the lower enthalpy of formation of NiSi compared to that for NiSi₂, it is reasonable to conclude that NiSi is the dominant species at the interface for the Ni coverage from submonolayer to continuous film. Spectroscopic evidence shows that the Ni silicides consist of only NiSi and NiSi₂ for the case of Ni deposition on a Si substrate at room temperature. We therefore conclude that the increases in the areal densities of B2 and B3 are due to an increased level of NiSi₂, the accumulation of NiSi, and a mixture of NiSi and NiSi₂.

Because of the finite inelastic mean free path (IMFP) of Auger electrons, AES is sensitive to chemical interactions that occur at the Ni/Si interface. Figure 3a shows Auger signals N(E) near the Ni M₂₃M₄₅M₄₅ Auger transition versus the kinetic energy (E) for Ni/Si(111) for different levels of Ni coverage; where N(E) corresponds to the counts of the AES measurements at kinetic energy E. For the case of 10 ML Ni/Si(111), it is sufficiently thick compared to the IMFP of Ni M₂₃M₄₅M₄₅ Auger electrons (~0.47 nm) and therefore the peak position of the Auger signals N(E) located at 57.0 eV is close to that of bulk Ni (grey solid line). For the case of thinner Ni/Si(111), the Ni M₂₃M₄₅M₄₅ Auger transition line shifts to a lower kinetic energy and the peak position of the Auger signals N(E) reaches 55.7 eV for 0.3 ML Ni/Si(111). Because Si is more electronegative than Ni, the
lowered kinetic energy of the Ni Auger transition line confirms the formation of Ni-Si compounds at the interface due to a change in the chemical environment of the Ni atoms from Ni-Ni to Ni-Si (grey dash line). We define the chemical shift of Ni M23M45M45 as the difference in the position of the peak for the Auger signals $N(E)$ respective to that for pure Ni. Figure 3b (black squares) shows the chemical shift for Ni M23M45M45 versus Ni coverage for Ni/Si(111) thicknesses less than 12 ML. For 0.3 ML Ni/Si(111), the chemical shift is as large as 1.3 eV, indicating that Ni silicide is formed at the interface. The chemical shift decreases with increasing Ni coverage. In order to explore the amount of Ni silicides at the interface, we propose a CSRC model based on analyses of the Auger peak position, as discussed below.

Figure 3. (a) Auger signals $N(E)$ near the Ni M23M45M45 Auger transition versus kinetic energy for 0, 0.3, 4 and 10 ML Ni/Si(111). (b) Chemical shift (black squares) and amount of Ni silicides (blue circles) versus Ni coverage for Ni/Si(111) thinner than 12 ML. (c) Schematic plots for simulated Auger peaks by assuming $\alpha$-$\alpha$ and $\alpha$-$\beta$ bonds with a layered structure.
where $d_{\text{tot}}$ is the layer thickness; $\lambda$ is the escape depth of the Auger electrons characterizing their IMFP in the solid; $I_0$ is the Auger sensitivity. We assume that the Auger sensitivity ($I_0$) is the same for both the $\alpha-\alpha$ layers and $\alpha-\beta$ layers. By considering an $\alpha-\beta$ compound layer covered by an $\alpha-\alpha$ layer, an $e^{-d_{\text{tot}}/\lambda}$ term can be added to Equation 3. The intensity $I_{\alpha\beta}$ is then expressed as

$$I_{\alpha\beta} = I_0(1 - e^{-d_{\text{tot}}/\lambda}) \cdot e^{-d_{\text{tot}}/\lambda}$$

(4)

The resulting Auger signal related to the thickness $d_{\text{tot}}$ for $\alpha-\alpha$ layers and $d_{\text{tot}}$ for $\alpha-\beta$ layers can be represented as

$$\gamma_s = \gamma_{\alpha\alpha} + \gamma_{\alpha\beta} = I_0(1 - e^{-d_{\text{tot}}/\lambda})e^{-E^2} + I_0(1 - e^{-d_{\text{tot}}/\lambda}) \cdot e^{-d_{\text{tot}}/\lambda} \cdot e^{-(E+\phi)^2}$$

(5)

As shown in Equation (5), the Auger peak position ($E_p$) can be obtained from the maxima value of the mixed Auger signal ($\gamma_s$) within the critical thickness of $\alpha-\alpha$ and $\alpha-\beta$ bonds.

$$\frac{d\gamma_s}{dE}_{E=E_p} = -2I_0 \cdot [E \cdot (1 - e^{-d_{\text{tot}}/\lambda})e^{-E^2} + (E + \phi) \cdot (1 - e^{-d_{\text{tot}}/\lambda}) \cdot e^{-d_{\text{tot}}/\lambda} \cdot e^{-(E+\phi)^2}]_{E=E_p} = 0$$

(6)

The Auger peak position $E_p$ follows the Equation

$$\frac{(1 - e^{-d_{\text{tot}}/\lambda}) \cdot e^{-d_{\text{tot}}/\lambda}}{(1 - e^{-d_{\text{tot}}/\lambda}) \cdot e^{-d_{\text{tot}}/\lambda}} = \frac{E_p + \phi}{E_p} e^{-(2E_p+\phi)\phi}$$

(7)

and is related to the chemical shift in AES measurements associated with compound layers with thickness $d_{\text{tot}}$.

Based on Equation (7) with the constraint of the total coverage of Ni, we simulated the thicknesses of Ni-Ni layers and Ni-Si layers to match the chemical shift obtained in AES measurements as shown in Equation 7. The thickness of the NiSi layer can be assumed to represent the amount of Ni silicides. The simulated results for the amount of Ni silicides are shown in Fig. 3b as indicated by blue circles. The calculated amount of Ni silicides increases rapidly with increasing Ni coverage and reaches a saturated value around 1.8 ML. By assuming the existence of a layered structure of a Ni-Ni layer over a NiSi layer as illustrated in Fig. 3c, the simulated results for the amount of Ni silicides for a 1.8 ML thickness is in good agreement with the experimentally obtained thickness of the magnetic dead layer shown in Fig. 1e.

After summarizing the STM, AES and SMOKE results regarding the morphologies, chemical states and related magnetic properties, we can now revisit the schematic plots in Fig. 1e where three phases are resolved for different coverage regimes. For regime I (0 to 1.8 ML), a nonmagnetic behavior is observed, as indicated by the nonzero value on the coverage axis from the straight-line extrapolation of the SMOKE data, and is confirmed by both dark spots in the STM images and NiSi bond states by AES. In regime II (1.8 to 5 ML), no Kerr intensity is detectable (Fig. 1e) while the chemical state is transformed from Ni-Si to Ni-Ni as demonstrated by the AES findings in Fig. 3. The observation of nano-sized clusters with oval shapes by STM (Fig. 1b) is indicative of the formation of clusters with lowered Curie temperatures. In Regime III for a Ni coverage above 5 ML, ferromagnetic Ni films are maintained.

Because of the high reactivity of a fresh Si surface, one possible route to passivate the Si surface so as to prevent chemical reactions between overlayers with the substrate is the insertion of an immiscible element. As an example of Co/Si(111), one possible route to passivate the Si surface is to insert Ag at Co/Si(111) surfaces to prevent the formation of Co-Si layers to match the chemical shift obtained in AES measurements as shown in Equation 7. The thickness of the NiSi layer can be assumed to represent the amount of Ni silicides.
consistent with the quenched magnetic moments of the first layer due to electronic coupling effects as reported for Ni/Ag(111)\textsuperscript{48}. For Ni/Si(111) without a Ag inserted layer, the thickness of the nonmagnetic layer is 1.8 ML. Because a 2.8 ML layer of Ag cannot completely cover the Si(111) substrate\textsuperscript{17}, the nonmagnetic layer is predicted to be between 1.8 and 2.0 ML for Ni deposited on 2.8 ML Ag/Si(111) if we consider the areal contributions of the Ni silicide and the Ni/Ag interface. In the case of Ni on the Si(111) surface that is not completely covered by Ag, it was surprising to find that the amount of nonmagnetic layer is significantly enhanced to 2.4 ML, as shown in Fig. 4b. Because the position of the Auger transition line for a submonolayer of Ni on 2.8 ML Ag/Si(111) is close to that on pure Si(111), the nonmagnetic layer is related to the formation of Ni silicides. The enhancement in the amount of the nonmagnetic layer shows that the Ag atoms serve as a catalyst to accelerate the chemical interaction of Ni and Si atoms to form Ni silicides.

From the experimental evidence showing a large chemical shift for submonolayer Ni on a few ML Ag/Si(111) (Fig. 4a), the formation of Ni silicides (Figs 2, 3 and 4a), and the enhanced dead layer (Fig. 4b), an interaction transferring mechanism for silicon atoms across the Ag layer is proposed to explain the enhanced silicide formation that occurs at room temperature. Schematic plots to elucidate the distribution of different species after Ni deposition showing an enhanced silicide formation are depicted in Fig. 5. From the discussions of formation enthalpies $\Delta H_{Ag-Si}$, $\Delta H_{Ni-Ag}$, and $\Delta H_{Ni,Si}$, the formation of Ag-Si particles plays a key role in enhancing silicide formation.
formation. Details of this are as follows. The rationale starts with the deposition of Ag on Si(111), as shown in Fig. 5a. A few MLs of Ag on the top of the Si(111) accumulate, with clusters being formed, as shown in Fig. 5b. The enthalpy of formation $\Delta H_{\text{Ag-Si}}$ is a negative value ($-5.9$ kJ/mol)\(^5\). From the thermodynamics point of view, the formation of Ag-Si bonding at the interface as well as the edges of the Ag islands is preferred after the deposition of Ag on Si(111) (Fig. 5c). The formation of Ag-Si particles plays a key role in enhancing silicide formation. For Ni deposited on the top of the submonolayer Ag/Si(111), Ni atoms can be adhered either on Si(111) patches or on the top of the Ag islands (Fig. 5d,e,g). Because of the high reactivity of the Si(111) surface, Ni silicide formation occurs on the Si(111) patches (Fig. 5f,h). On the top of the Ag islands, Ni-Si bonding is dominant as compared to Ni-Ag bonding because of the large negative enthalpies of formation for Ni silicides ($\Delta H_{\text{NiSi}} = -29.3$ kJ/mol, $\Delta H_{\text{NiSi}_2} = -38.7$ kJ/mol)\(^5\). The interaction transfer occurs for Si atoms via Ag-Si bonding, un-bonded from Ag-Si, and finally bonding with Ni to form Ni silicides. This scenario causes the formation of Ni silicide on Ag clusters to be substantially enhanced (Fig. 5f,h,i) as evidenced by the large chemical shift shown in Fig. 4b.

**Conclusion**

At the initial stage of Ni deposition on a Si(111) surface, dark defects with different sizes are observed and are related to the different chemical states of Ni silicides. This can be attributed to the strong bonding between Ni and Si atoms, NiSi is the relatively dominant species at the Ni/Si interface. Assuming that a Ni layer is formed over a NiSi layer with the total coverage as a constraint, we established a CSRC model that represents a practical method for determining the amount of ultrathin Ni silicides that are produced at the buried interface. Based on the morphologies, the chemical states and related magnetic properties of Ni/Si(111), the phases of nonmagnetic Ni silicides, Ni clusters with lowered Curie temperatures and ferromagnetic Ni films were resolved for different coverage regimes. For a submonolayer Ni deposited on a few monolayers of Ag/Si(111), the chemical state of Ni was found to be closer to that for Ni silicides rather than for Ni-Ag bonding. The finding that the amount of the nonmagnetic layer is enhanced shows that the Ag-Si particles serve as a catalyst that promotes the chemical interaction of Ni and Si with the formation of Ni silicides. An interaction transferring mechanism for silicon atoms across the Ag layer is proposed for the enhanced silicide formation. Based on the formation enthalpies $\Delta H_{\text{Ag-Si}}$, $\Delta H_{\text{Ni-Ag}}$, and $\Delta H_{\text{Ni-Si}}$, Ag-Si particle formation plays a key role in enhancing silicide formation via a specific interaction transfer mechanism at room temperature. The data and related mechanisms reported herein provide insights into strategies for producing ultrathin silicides at a buried interface.

**Methods**

All experiments were performed under ultrahigh vacuum (UHV) conditions with a base pressure of around $1 \times 10^{-10}$ torr. The Si(111) substrate was cleaned by repeated Ar$^+$ ion bombardment and annealing treatments at 1250 K until a well-ordered 7 × 7 structure was obtained, as evidenced by STM and LEED. The LEED pattern and STM image for Si(111)-7 × 7 structure can be found in our previous report\(^1\). The purity of the surface was checked using AES. Ni atoms were evaporated from a resistively heated, high purity Ni coil (99.997%). Ag atoms were deposited on the surface from a well collimated evaporator using Ag rods with a high purity (99.999%) as the Ag source. The coverage of an overlayer was determined from the ratio of the intensities of the overlayer and substrate atoms, and was double checked using a SYCON thickness monitor of a quartz balance. For overlayers on a Si(111) surface, one ML is equal to 0.08 nm as defined by the atomic density of substrate surface\(^4\)-\(^6\). A He-Ne laser with a wavelength of 632.8 nm was used as the light source for the SMOKE measurements. The experimental components have been described in previous reports\(^1\)-\(^5\),\(^12\),\(^22\),\(^23\).
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Acknowledgements
The authors wish to acknowledge financial support from Ministry of Science and Technology of ROC under Contract Nos. MOST 105-2112-M-003-007 and MOST 106-2112-M-003-010. This article was subsidized by the National Taiwan Normal University (NTNU), Taiwan.

Author Contributions
C.H.T.C., P.C.J. and Y.T.C. set up the measurement apparatus. C.H.T.C., P.C.J. and Y.T.C. carried out the experiments. J.S.T. planed and supervised the study. C.H.T.C. and J.S.T. wrote the manuscript with reviewing by H.L.H. and W.B.S. All authors participated in discussing the results and commented on the manuscript.

Additional Information
Competing Interests: The authors declare no competing interests.

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