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Surface plasmon resonance of the W nanowires

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Abstract

The Surface plasmon resonance (SPR) of metal materials has been widely used in photocatalysis, light sensing, biomarkers, solar cells and other fields. In this study, the surface plasmon characteristics of tungsten (W) nanowires with different diameters and lengths are analyzed using the finite element method. The thermal effect in the gap of crossed nanowires induced by the plasma resonance is studied. Results show that the resonance peak shifts red, and the resonance intensity increases with the increase in diameter. The increasing diameter results in decreasing electric field intensity and heat in the gap of the crossed tungsten (W) nanowires. The frequency of resonance peaks almost remains unchanged with increasing length. The two to six wave belly plasma modes are visible with increasing nanowire length. With exposure to incident light, the SPR in the shortened spacing results in increasing electric field intensity and the generated heat of gap between the two crossed tungsten (W) nanowires. Once the two crossed nanowires are welded, the heat production in the crossed part decreases, which indicates the self-limitation of plasma welding.

1. Introduction

Metal nanowires are widely used in the field of light due to their unique physical and chemical properties [1, 2]. To reduce the problem of large contact resistance at the nanowire junction due to the weak bonding between metal nanowires, some strategies have been reported, including mechanical pressing, heat treatment and medium introduction [3], which cause damage to the nanowires to varying degrees. Surface plasmon resonance (SPR) plays an important role in the interaction between nanostructures and light [4–6]. The plasma welding method is a room temperature, non-contact nano welding method that only uses light and does not need to apply any other forms of energy. It can accurately transfer energy to the position to be welded. After the formation of the solder joint, the energy suddenly decreases to prevent overheating. It can realize remote control of the internal heat generation of metal nanoparticles. When the eigenfrequency of the plasma element is the same as that of the incident light, SPR is generated. SPR properties are related to the shape and size of nanostructures [7–9]. SPR has broad application prospects in the fields of solar cells [10], sensors [11], surface-enhanced Raman scattering [12], LEDs [13], photodetectors [14], and nanoantenna [15].

Current research on the SPR influence is mainly focused on gold, silver, and other metal materials [16, 17]. Limited research exists on the thermal effect of plasma for W nanowires. Though tungsten is a brittle metal, it shows a surprisingly high flexibility on a nanoscopic scale and maybe used in flexible electrodes [18]. Research aims to know how the structure and morphology of W nanowires affect their SPR properties and further influence the thermal effect of SPR. Nevertheless, the existence of imaginary part of dielectric constant of metal materials will lead to electromagnetic wave absorption and loss characteristics. When the metal surface is excited by light, the free electrons collide with the surface or ionic lattice in motion, and then nonradiative decay of energy occurs, resulting in Joule heating [19, 20]. Through avoiding the use of nano-manipulators, in situ TEM, nanoindentation, and other precision equipment, and taking the advantage of the large field enhancement that occurs in the nanoscale gap between two crossed silver nanowires, a high-efficiency and high-quality method for
welding metallic nanowires has been realized [21, 22]. Researchers have used light sources to weld metallic nanowires [23–25].

In this work, the characteristics of SPR for W nanowires with different diameters and lengths are researched. The study of self-welding by plasma welding could improve the performance of W nanowire flexible electrodes by plasma welding in the future.

2. Experiments and methods

2.1. Experimental Procedure

W nanowires are prepared through selective etching of NiAl-W alloys [26]. The raw materials used in this experiment are Ni(99.99%), Ni-Al(99.99%), and Ni-W(99.99%) intermediate alloys, which are selected in accordance with the composition ratio of eutectic NiAl-1.5at%W. They are melted by high vacuum arc and wire cut into the required φ 7 × 90 mm sample. The polished and ultrasonically cleaned test bar is placed into a corundum tube, and Bridgman induction heating is applied for directional solidification. In the experiment, the temperature gradient of the heater is 300 K cm−1 at 1700 °C, and the GaInSn liquid metal is used for cooling. The NiAl-W alloy is directionally solidified at a growth rate of 2–25 μm s−1. Tungsten nanowire lengths of several microns to several hundred microns are obtained by corrosion at different times in a 3.2% HCL + 3% H2O2 mixed solution at a constant potential of 0.2 V.

2.2. Finite element method (FEM) models

FEM is used to simulate the electric field and heat generation process of W nanowires in different diameters and lengths. The crossed W nanowires are perpendicular to each other at 90°. The wavelength of incident light is from 100 nm to 1000 nm. The incident light is parallel and perpendicular to the axis of the W nanowires. The heat generation is determined by the electric field.

The simulation is carried out on the basis of the following assumptions:

1. Size-dependent nanowire plasma resonance. With reference to the absorption spectra and electric field analysis of different diameters and lengths of silver nanowires in finite-difference time-domain simulation [27], similar laws are found to verify the influence of different diameters and lengths of W nanowires on the plasma resonance frequency and mode.

2. Distance-dependent resonance coupling of cross-nanowire junction plasma. According to the plasma-coupled hybrid model [28, 29], when nanowires are close to each other, the surface electric fields of nanowires overlap, which splits the plasma into two new resonances: low-energy bonding mode and high-energy antibonding mode. From the cross-analysis of silver nanowires, the electric field in nanogap is much larger than that around single nanowires. In accordance with Joule’s law, nanowire surface welding is realized by heating up the local electric field between the two nanowires. To explore the ‘zipper effect’ [21], the self-limiting characteristics and related mechanism of plasma welding W nanowires are determined.

3. Results and discussion

Figure 1 illustrates the morphologies of elliptical W nanowires grown in 8 μm s−1 after selective etching the NiAl matrix. The obtained W nanowires are orderly arranged and have dozens to hundreds of microns with a diameter of 220 nm. The diameter and the space of the W nanowires depend on the growth rate and temperature gradient. W nanowires with a diameter of 180–320 nm can be obtained at a proper growth rate [26]. Meanwhile, the length of W nanowires can be controlled by the etching time.

3.1. Influence of nanowire diameter on localized SPR (LSPR)

Figure 2(a) shows the absorption spectra of W nanowires obtained in different diameters. Figure 2(b) demonstrates the corresponding resonance peak positions and intensities. The resonance intensity increases with increasing W nanowire diameter. When the wavelength of W nanowire is comparable to its diameter, the W nanowire has only one resonance peak at 160 nm wavelength. When the diameter of W nanowires exceeds 200 nm, the absorption spectra display two resonance peaks, which correspond to two resonance modes. One is the high-frequency resonance perpendicular to the axis of nanowires, corresponding to a wavelength of 160 nm. The other is the low-frequency plasma resonance along the nanowire axis, corresponding to a wavelength of 675 nm [30]. As shown in figures 2(a) and (b), the resonance peak shifts red with the increase in W nanowire diameter, which is consistent with the research of other scholars [31]. The resonance intensity increases with increasing diameter. Figure 3 shows the distribution of electric field in xy plane, which corresponds to the
wavelengths of 675 and 160 nm for the W nanowires. When the wavelength is 675 nm, the electric field on the surface of W nanowires presents two abdominal waves. When the wavelength is 160 nm, the electric field focuses on the surface of W nanowires. Obviously, the intensity of electric field increases as the wavelength increases from 160 nm to 675 nm. Figure 4 shows the distribution of electric field in xy plane for different diameters of W nanowires. The electric field mainly focuses on the gap between the crossed W nanowires. The increase in
diameter results in decreasing electric field intensity of the gap between the crossed W nanowires. Figure 5 shows the generated heat of W nanowires in different diameters. The generated heat intensity in the gap of two crossed nanowires decreases with increasing diameter because the melting point of W nanowires with larger diameters is high, the required welding heat is large, and the plasma resonance self-limiting welding effect is weak.

3.2. Influence of nanowire length on LSPR

Figure 6 (a) shows the absorption spectra of W nanowires obtained in different lengths. Figure 6 (b) demonstrates the corresponding resonance peak positions and intensities. As shown in figure 6 (a), both the low-frequency and high-frequency resonance peaks almost remain unchanged with increasing length. Meanwhile, the resonance intensity first increases and then decreases with increasing W nanowire length, and it reaches the maximum at the nanowire length of 700 nm. Figure 7 illustrates the distribution of electric field in xy plane corresponding to a wavelength of 675 nm of the W nanowires in different lengths. The simulated absorption spectra indicate that with the increase in nanowire length, two to six wave belly plasma modes are visible [32]. This result demonstrates that the size of nanowires has a significant impact on the frequency and mode of plasma resonance. Therefore, the mode and frequency of plasma resonance can be adjusted by controlling the morphology of nanowires.

Figure 4. Distribution of electric field in xy plane corresponding to a wavelength of 675 nm of perpendicularly crossed W nanowires with different diameters. The length of W nanowires is 1000 nm and the gap is 2 nm.
3.3. Influence of distance between crossed nanowires on LSPR

The surface plasmon coupling of crossed nanowires plays an important role in nanowire welding. The distribution of electric field of perpendicularly crossed W nanowires in different spacing is shown in figure 8. When the spacing of crossed nanowires is more than 4 nm, the distribution of electric field between the two crossed nanowires is weak. As the spacing decreases to 2 nm, the electric field focuses on the gap of the crossed nanowires. When the spacing is closer, the gap electric field is focused on the nanogap of the crossed nanowires and becomes more intensive. When the two nanowires are about to contact (the gap size is 0 nm), the gap heat reaches the maximum value. If the nanowire nodes start to melt, the junction of the nanowires starts to weld. The gap plasma of the two nanowires is no longer excited, and the gap heat decreases rapidly. When the heat generated is inadequate to fuse the nodes, the welding is terminated. The gap electric field is limited at the crossed region and thus performs self-limiting welding [21, 22]. As shown in figure 4, the larger the diameter is, the weaker the electric field will be. The reason is that a larger diameter requires higher heat to melt the nanowires. However, the weak coupling electric field between large-diameter nanowires may lead to a weak plasma resonance effect, which may result in the poor plasma self-limiting welding performance of large-diameter nanowires [33].

A concentrated gap field generated by the coupling electric field of metallic nanowires can be expressed as follows [34]:

![Figure 5](image1.png)

**Figure 5.** Heat of crossed nanowires with diameters of 280, 300, and 320 nm. The scale bar is 150 nm.

![Figure 6](image2.png)

**Figure 6.** (a) Absorption spectra of W nanowires with a diameter of 200 nm obtained in different lengths, (b) Variation in formant positions and intensities with different lengths.
where $E$ is the scattered electric field, $E_0$ is the electric field of the incident light, $\varepsilon$ and $\varepsilon_1$ are the frequency-dependent permittivity of the air and metallic nanowires, $a$ is the nanowires radius, and $d$ is the distance from the nanowires center.

Figures 4 and 8 illustrate that with the increase in $a$ and $d$, the gap electric field apparently decreases. The local electric field caused by the LSPR may result in local hot spots at the gap between the two crossed nanowires.

The light-induced heat generation can be expressed as follows [19]:

\[ E = E_0 \frac{\varepsilon_1 - \varepsilon d^2}{\varepsilon_1 - \varepsilon_2 d^2} \]  

(1)

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**Figure 7.** Distribution of electric field in $xy$ plane corresponding to a wavelength of 675 nm of W nanowires in different lengths.
where \( q \) is the volumetric heat source density, \( \omega \) is the angular frequency of field, and \( E \) is the electric field. Equation (2) illustrates that the generated heat is proportional to the square of the electric field.
Figure 9 shows the heat generation in different spacing of W nanowires. With the decrease in spacing, the electric field of the gap between two crossed nanowires increases, while the generated heat enhances. Once the heat is enough to melt the nanowires, local welding forms, which produces a local connection. Afterward, the hot spot moves to the unclosed gap [19]. During the plasma welding process, hot spots form at the edge of the gap and migrate to the outside, which is called the zipper effect [21]. When the two nanowires are welded together, the electric field in the cross part and the heat production decreases, resulting in the self-limitation of plasma welding. When the plasma is applied to the crossed nanowires, the cross section can be locally heated, leading to the junction of the two contact nanowire surfaces, to avoid the breakage of the nanowires in the nonwelding position caused by the overall heating of the nanowires [35]. This self-limited welding can significantly improve the performance of flexible electrodes.

4. Conclusions

(1) The resonance peak shifts red with the increase in W nanowires diameter. The increased diameter results in the increasing resonance intensity and the decreasing electric field intensity and generated heat of the gap between crossed W nanowires.

(2) Both the low-frequency and high-frequency resonance peaks almost remain unchanged with the increasing length. With the increase in nanowire length, two to six wave belly plasma modes are visible. The mode and frequency of plasma resonance can be adjusted by controlling the morphology of W nanowires.

(3) The shortened spacing results in increasing electric field intensity and generated heat of the gap between perpendicularly crossed W nanowires. The movement of hot spots forms the zipper effect. When the two
nanowires are welded together, the electric field in the cross part and the heat production decreases, resulting
the self-limitation of plasma welding for the W nanowires.

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Data availability statement

No new data were created or analysed in this study.

Conflicts of interest

The authors declare no conflict of interest.

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