27405

Preservation and Conservation of Archaeological Sites and Artefacts in Malaysia

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Introduction

Archaeological sites and artefacts are among the most vulnerable of human cultural heritage that have suffered extensive damages. Excavations of archaeological sites and the removal of artefacts from sites have often caused abrupt changes to their ambient preserving conditions. As most archaeological sites and artefacts are already in the advanced state of deterioration, exposure to high temperature and high relative humidity, especially in Asian countries like Malaysia, can and have caused further damage to our cultural heritage. Other factors such as air pollution, chemical action of light, and bio-degradation caused by fungus and insect attack have also brought about the deterioration of these materials. In recent years, the preservation and conservation of archaeological sites and artefacts in Malaysia have come under another threat of destruction due to the rapid pace of development in the country. This paper discusses and compares the various achievements, issues and problems of conservation of archaeological sites and artefacts in Malaysia. This paper discusses and compares the various achievements, issues and problems of conservation of archaeological sites and artefacts in Malaysia. Discussions will be focused on several case studies of conservation of archaeological sites and commonly excavated artefacts such as stone artefacts, pottery and ancient human skeletons in Malaysia.

Conservation of Archaeological Sites

In Malaysia, most of the archaeological sites discovered in the country have been cave or rockshelter sites in limestone hills because tropical field conditions often made it difficult to locate open sites. In any case, archaeological sites are often discovered in an advanced state of deterioration that their protection and preservation becomes a challenging task. In the past, particularly the last 10 years or so, many archaeological sites have been subjected to constant threat of destruction due to the rapid pace of development in the country. Sites have been uncovered and damaged during major digging works such as the construction of highways, roads, opening of farmlands, building of dams, and housing estates. Cave sites that contained archaeological evidence were destroyed by guano digging and quarrying activities. For example, cave sites such as Gua Badak in Lenggong, Perak that contained ancient charcoal drawings was destroyed during quarrying activities. Limestone hills with prehistoric cave sites were also destroyed during the construction of a dam at Kenyir Lake in Ulu Terengganu. Between 1978 and 1985 when the area was flooded with water, several caves of archaeological importance were believed to have been lost underwater (Price 2002).

The awareness of the importance and the need to save the country's cultural heritage from further destruction had become increasingly apparent during the last 10 years or so. During this period, some major projects in the country had began to include archaeology in their Environmental Impact Assessment studies, for examples archaeological impact assessment of the Petronas Gas Utilisation Project in Peninsular Malaysia in 1989 and the construction of the Bakun Dam in Sarawak in 1994. Several megalithic sites in the Negri Sembilan–Melaka area were excavated and relocated to Kuala Lumpur during the construction of the Petronas Gas pipelines (Zuraina 1993). During the construction of the Bakun dam in Sarawak, an ancient habitation area was excavated and many old burial grounds of the communities affected by the construction of the dam were identified and some were exhumed and relocated to resettled areas.

In 1996, the palaeolithic site of Bukit Jawa in Lenggong, Perak was uncovered accidentally during the construction of the Kuala Kangsar – Grik highway. A villager who had worked with us for several years reported findings of stone tools during the highway construction. Consequently, the Department of Museums and Antiquity with the cooperation of the Road Works Department halted the construction of the highway for a period of more than one month in order to allow the archaeological team from the University of Science Malaysia, Penang to conduct rescue excavations and to collect data and artefacts at the affected areas in Bukit Jawa (Zuraina 1997).

Conservation of Archaeological Artefacts

Archaeological surveys and excavations in Malaysia often uncovered prehistoric sites used for habitation, temporary camp, burial or stone-tool making. These sites often contain prehistoric remains such as stone artefacts, pottery, human skeletal remains, food remains – animal bones and shells, ornaments or metal objects. These archaeological artefacts are seldom recovered in well-preserved state as they are subjected to years of chemical and biological attacks during burial. In order to recover and in some cases to save the artifacts, conservation treatment may be required in the field as well as in the laboratory. The following discusses a number of conservation methods commonly used to treat archaeological artefacts such as stone artefacts, pottery, and human skeletal remains in Malaysia.

Stone artefacts such as pebble and flake tools made of quartzite, quartz, chert, sandstone, agate and obsidian are often found in rather good condition due to the durable nature of these rock materials. As such, they usually do not require special handling and can be cleaned with water and a soft brush. However, special precautions were exercised for tools that might have residue or gloss on their cutting edges. Such tools are usually not washed because they have to be examined in the laboratory in order to gain information on their uses or functions.

Pottery is often found in the form of earthenware shards at habitation sites or sometimes in the form of complete pots as mortuary objects in burial sites. The majority of these well-fired shards can be washed with water and a soft brush, except shards that might contain remains of food or liquid. All shards from the same pot should be kept together after removal from the ground. This will help facilitate the refitting of the pots. Complete pots are carefully removed and its contents sampled or removed together with the pot for analysis at the laboratory. Broken pieces of shards are refitted with adhesives such as UHU or preferably Paraloid B72. The edges of the shards to be joined should be cleaned thoroughly and dried before applying these adhesives, and missing portions of the pots are often filled with the plaster of Paris.

Human skeletal remains in Malaysia, on the other hand, are often recovered in a poor state of preservation. This is mainly because long-term burial of human remains usually leads to damages caused by chemical and biological attacks. For example, the 4,000 years old archaeological site of Gua Harimau, Perak – a prehistoric cemetery cave site with more than 11 human skeletons buried with mortuary objects (Zolkurnian 1989). The skeletons were found in highly deteriorated condition and in very fragile state because the cemetery was located at the mouth of the cave, which was exposed to rain and much sunlight. The bones were found fused with calcium carbonate (lime) from the cave, making it difficult to distinguish between limestone and bones. In such cases, chemical tests were conducted in the field to help identify bones. Removal of the skeletal remains was also a major problem as they are very fragmentary and some had to be removed intact with the soil to preserve their structures.

In 1990, one of the oldest and most complete human skeletal remains in Malaysia and Southeast Asia was discovered at Gua Gunung Runtuh, Lenggong, Perak (Zuraina 1994). The skeleton, named the "Perak Man", was radiocarbon dated as old as 10,000 years ago. The Perak Man's skeleton was preserved for such a long period of time because it was buried in a relatively dry cave (2% moisture), with a constant temperature of 24 degree Celsius and a constant relative humidity of 89% (Stephen 1994). However, due to the rather fragile condition of the skeleton and the inaccessibility of the site (it was located about 75 meters in a limestone hill at the fringes of the forests), every pieces of the skeleton had to be removed individually. The rib cage, spinal column, and the pelvic region were very fragile and had to be consolidated with 5% polyvinyl acetate in acetone. The spinal column needed extra consolidation with wrappings of several layers of bandages coated with the plaster of Paris. Small breaks were mended with UHU before removal and highly fragmentary bones such as the shoulder blade had to be removed with the aid of a shaped block of plasticine. After evacuation from the cave to the base camp, the temporary consolidant of plaster of Paris was removed and the skeletal remains were cleaned mechanically with wooden sticks, water and a weak acetic acid (5%) to remove stubborn dirt and lime encrustations. The skeletal remains were air-dried and re-assembled, and a new stable environment was created to preserve the skeleton. The skeleton is now preserved in a humidity controlled glass cabinet with 24 hour air-conditioning at a constant temperature of 20 degree Celsius and a constant relative humidity of 45%. The preservation condition of the skeleton had thus far remained stable, without any visible deterioration for more than 12 years.

Preservation and Conservation Issues and Problems

Archaeological sites and artifacts are protected under separate laws in three different regions in Malaysia, namely Peninsular Malaysia, Sabah and Sarawak. In Peninsular Malaysia, they are protected under Akta 168 of the Antiquities Act 1976, which provides for the control, preservation, and study of ancient and historical monuments, prehistoric sites, prehistoric and historic artifacts as well as matters related to trade and export of prehistoric and historic artifacts. Under this act, the approval from the Department of

Museums and Antiquity is needed in order to excavate archaeological sites and artifacts. In Sabah and Sarawak, the Sabah and the Sarawak Cultural Heritage Ordinance 1993 protect the archaeological sites and artefacts –these ordinances provide provisions for the preservation of antiques, monuments and sites of cultural, archaeological, architectural, artistic, religious or traditional interest or value for the benefit of the state and as a heritage of the people.

Despite these protective laws, however, there are still areas that can still be improved, for example the inclusion of archaeology in an Environment Impact Assessment study need to be made mandatory before the construction of major highways and dams, clearing of large agricultural land as well as quarrying and guano digging activities. Another problem is the lack of awareness on the importance of preserving cultural heritage in Malaysia, for example at Gua Badak in Perak, the the Department of Land Survey approved the quarrying of the limestone hill that contained prehistoric cave paintings – parts of it was destroyed before it was reported to the Museum and action was taken to stop the project. In addition, almost all sites with cave painting in Malaysia also suffered from graffiti. In the highlands of Bario in Sarawak, megalithic stone structures were under threat of being destroyed due to changing religious values – the Kelabits embraced Christianity and denounced the worshipping of these stone structures. It is clear that the present laws are not enough to protect archaeological sites from destruction, especially in the process of rapid development in Malaysia. As such the Department of Museums and Antiquity Malaysia is currently pushing for amendments to the Antiquities Act 1976 to save our cultural heritage, following the poor preservation of artefacts. The amendments would cover gazetting and the control of historical buildings and sites from intrusion, destruction as well as control of treasures and sunken vessels. This is also to ensure that valuable artefacts are not stolen or damaged. Heavier penalties will be imposed on offenders if the proposals are approved. In Malacca in Nov 2002, two heritage buildings at Jonker Street were brought down by their owners, despite a reminder from the local council not to do so. The proposals will also grant more power to the state government to protect and to monitor historical sites and sunken vessels.

Another preservation and conservation problem in Malaysia is the lack of well-trained conservators with good scientific knowledge and skills to solve preservation and conservation problems of artefacts. At present, museum technical staff conducted mostly basic cleaning and maintenance of archaeological sites and artefacts. The task of saving and conserving archaeological sites and artefacts have been made more challenging by the hot and humid climate, which often speed up the process of deterioration of sites and artefacts. During archaeological excavations, fragile artefacts that need immediate on-site attention are often not given preservation and conservation treatment. The most common reason is the time constraints and the lack of conservation expertise during fieldwork. Instead, dry cleaning or cleaning with water is generally done at the site. Conservation after excavations usually involves preventive treatment - cleaning and treating artifacts to reduce the rate of deterioration. Rarely will curative conservation or restoration be carried out unless for display purposes. These artefacts are later brought back to the laboratories and whether or not conservation treatment of these finds will be carried out depends on the importance of the finds and again the availability of technical expertise. It is common practice that most archaeological finds will only undergo basic cleaning etc and later studied or go on display or end up in the store rooms of museums.

In addition, the lack of storage space in museums or universities as well as the poor preserving conditions for artefacts still remain a huge problem in Malaysia. Every year, considerable amount of artefacts are recovered from archaeological surveys and excavations and this had created much storage problems. Due to the lack of storage space, most artefacts often end up in boxes. The environment of museums display and storage are often not conducive for preservation of artefacts. For example, air-conditioners are only turned on during office hours (about 8 hours a day) resulting in wide fluctuations of temperatures and humidity.

Conclusions

Given the increased threat of archeological site destruction due to the rapid pace of development in Malaysia, one of the most important issues that needs to be addressed is surely the level of awareness of the importance of preserving and conserving archaeological sites and artifacts in the country. There is an urgent need to educate or increase awareness among the public and the relevant authorities regarding the importance of protecting sites and artifacts. Given the problems and difficulties of conserving, presenting and maintaining *in-situ* archaeological sites, perhaps not all archaeological sites should be preserved or protected for exhibition to visitors or scholars. Only sites that are considered important enough for displays should be preserved and conserved for future generations. Sites that are less important should be backfilled after excavations in order to protect them. Archaeological artifacts that need immediate attention should be treated during fieldwork with the help of a trained conservator. This means more personnel should be trained in the field of conservation in Malaysia. Special displays and storage rooms with controlled humidity and temperature should be built for important archaeological finds. It is commendable that the Department of Museums and Antiquity is currently taking steps to review and amend laws that will further protect sites and artefacts in the country. More importantly, cooperation between archaeologists and conservators is needed in order to minimize structural and compositional changes to the original archaeological sites and artefacts and therefore preserve information that they might contain about the prevailent past.

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27288

Low applied bias for p-GaN electroluminescent devices

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Abstract

Nickel ohmic contacts and Schottky contacts using silver or titanium were fabricated on Mg-doped p-GaN films. The light emission has been obtained from these thin film electroluminescent devices (ELDs). These ELDs were operated under direct current (DC) bias. Schottky and ohmic contacts used as cathode and anode were employed in these investigations. Alternatively, two Schottky contacts could be probed as cathode and anode. Both ELDs were able to emit light. However, electrical and optical differences could be observed from the two different probing methods. ELDs started to emit light under forward bias of 3V at room temperature in a dark environment. The change of light color from yellowish white, green, blue to violet could be observed when the potential between the electrodes was increased gradually. The light intensity emitted increased with the applied bias. Electrical properties of these ELDs were characterized by current-voltage (I-V) system, the barriers heights determined from the I-V measurements were found to be related to the electroluminescence.

1. Introduction

The nitride semiconductors such as InN, GaN and AlN and their alloys have long been viewed as highly promising semiconductor materials for their practical applications in short wavelength optoelectronic devices and high power/high frequency/high temperature electronic devices. These excellent applications are based on the unique and superior properties of nitride semiconductors such as wide direct bandgap, strong piezoelectric effects (~0.2 – 0.6 GV/m), high-saturation velocity (~2.7×10^4 cm/s) and high-breakdown field (~0.2×10^9 V/m) [1]. The nitride semiconductors form a continuous alloy system with direct band gaps ranging from 1.9 eV for InN, to 6.2 eV for AlN with 3.4 eV for GaN. Therefore light emitting devices fabricated from III-V nitrides are active at wavelength ranging from green to ultraviolet.

The evolution of nitride semiconductors has been challenging. Following the epitaxial synthesis of GaN, a flurry of activities sprung up to explore this material for light emitting devices. In the early development stage, p-type GaN was not achievable due to high background electron concentration which was attributed to nitrogen vacancies, subsequently, the interest of the research and development in this semiconductor was waning rapidly mainly because of the failure in obtaining the p-type GaN, and the poor crystal quality. The first blue LED was fabricated by Pankove *et al* [2] in 1972. That was metal/Zn-doped highly resistive i-GaN/ undoped n-GaN (M-i-n) structured light emitting device. In this device, electrons were injected from the metal under a forward bias into the i region formed by Zn doping, dropped to Zn centers and blue light was generated.

Light emitting devices which can change the emission colour by varying the electrical bias are potentially used for indicators and backlighting which can indicate two different conditions i.e. the status of "on" or "off". The common approach used to obtain multiple colours is colour-by-white [3, 4], in which red, green and blue (RGB) colour filters are employed to selectively create saturated RGB colours from the white light; and techniques for integration of side-by side single colour RGB devices [5]. However, this device requires bias control of three or more electrodes.

Light emitted from the Schottky contacts on p-type GaN films are rarely investigated and explored thus far. In this paper, we report on the light emission of electroluminescent device (ELD) based on p-type GaN. These ELDs were operated under direct current (DC) bias. ELDs started to emit light under forward bias of about 3V at room temperature in a dark environment. The change of light colour from yellowish white, green, blue to violet could be observed when the potential between the electrodes was increased gradually. Since the device structure is generally simple and requiring only two electrodes, in addition, the change of emission colours could be induced by the change of applied voltage; therefore the device could have some practical applications as indicators or backlighting.

2. Experimental

Mg-doped p-type GaN film grown on sapphire substrate with hole concentration of ~5×10^{17} cm^{-3} was used in this study. The thickness of the p-GaN film is 4 μm. The resistivity was measured and found to be 65 Ω-cm. Prior to the metallization, the native oxide was removed in the NH_4OH: H_2O = 1:20 solution, followed by HF:H_2O = 1:50. Boiling aqua regia (HCl: HNO_3 = 3:1) was used to chemically etch and clean the samples.

After surface treatment, Ni was first deposited onto the p-GaN as ohmic contacts by a sputtering system. The samples with the ohmic contacts were then annealed under flowing nitrogen gas environment in the furnace at 400°C for 15 minutes. The ohmic behaviour of the contacts was checked and confirmed by I-V measurement.

Subsequent to the ohmic contacts deposition, the samples were divided into two sets. For the first set of samples, Ag was sputtered onto the p-GaN films via a metal mask to form the Schottky contacts. On the other hand, Ti was coated as Schottky contacts for the second set of samples. The metal mask which was used for Schottky contacts fabrication consists of an array of dots with diameter of 250μm. The top and cross section views of the ohmic and Schottky contacts of a typical sample are shown in Fig. 1.

2.1 Probing conditions

First set of samples comprises Schottky contacts made of Ag: The first sample (Ag1), cathode and anode were connected to Schottky and ohmic contacts respectively, whereas for the second sample (Ag2), two Schottky contacts were probed as cathode and anode. On the other hand, both ohmic contacts were probed as cathode and anode for the third sample (Ag3). Second set of samples consists of Schottky contacts coated with Ti, the probing conditions for first sample (Ti1), second sample (Ti2) and third sample (Ti3) were similar to the first set of the samples. The samples were then electrically characterized by an *I-V* system under different probing conditions as above-mentioned. The data were collected at room temperature and in a dark environment.

3. Results and discussion

Fig.2 (a) and (b) show the I-V characteristics of two sets of samples. Sample Ag1, Ag2, Ti1 and Ti2 exhibit typical Schottky behaviour, whereas Ag3 and Ti3 show an ohmic characteristic.

Schottky barrier heights, SBH, can be determined by I-V measurements. For thermionic emission and V>3kT/q, the general diode equations are [6]:

$$I = I_o \exp\{qV/(nkT)\} \qquad (1)$$

$$I_o = A^*AT^2 \exp\{-q\, \Phi_B/(kT)\} \qquad (2)$$

As usual, I_o is the saturation current, n is the ideality factor, k is the Boltzmann's constant, T is the absolute temperature, Φ_B is the barrier height, A is area of the Schottky contact and A^* is the effective Richardson coefficient. The theoretical value of A^* can be calculated using

$$A^* = 4\pi m^* q k^2/h^3 \qquad (3)$$

where h is Planck's constant and $m^* = 0.80m_o$ is the effective hole mass for GaN [7]. The value of A^* is determined to be $103.8\ Acm^{-2}K^{-2}$.

The plot of *ln I vs V* will give a straight line with a slope of $q/(nkT)$, and the intercept with y-axis will yield I_o, in which barrier height, Φ_B can be obtained using Eq. (2). The SBHs of sample Ag1 and Ti1 were both determined to be 0.52 eV.

On the other hand, for samples involving two Schottky contacts (i.e. sample Ag2 and Ti2), representing two diodes connected back-to-back, the *I-V* characteristics of the Schottky contact are more appropriate to be analyzed in the more general form of equation, where it can be used under reverse bias conditions [8, 9]

$$I = I_o \exp(qV/\{nkT\})[1-\exp(-qV/\{kT\})] \tag{4}$$

The equation can be written as

$$\frac{I\exp(qV/\{kT\})}{\exp(qV/\{kT\})-1} = I_o \exp(qV/\{nkT\}) \tag{5}$$

Based on equation (5), the plot of $In\{I\exp(qV/\{kT\})/[\exp(qV/\{kT\})-1]\}$ *against* V will give a straight line, similarly, I_o is derived from the intercept with y-axis, in which SBH, Φ_B can be calculated using Eq. (2). The SBHs of sample Ag2 and Ti2 were deduced to be 0.45 eV and 0.40 eV respectively.

When electrical bias was applied on these samples, light emission was observed for Ag1, Ag2, Ti1 and Ti2. Similar to M-i-n structured light emitting device reported in early 70s [10], the light was emitted only from the cathode, and the active region was the area underneath the metal contact. On the other hand, no light emission was found for Ag3 and Ti3.

Sample Ag1, started to emit yellowish white light under 3.2V, followed by green light at 8.0V, eventually the blue-violet emission at 16.0V. For sample Ag2, similar observation was found at 2.6V, 6.5V and 15.0V. On the other hand, samples with Ti

Schottky contacts were found to have a higher voltage for electroluminescence to take place. Sample Ti1 began to emit at 7.5V for yellowish white light; followed by green and blue emissions, which were produced at 16.5V and 19.0V respectively. However, for sample Ti2 such emissions were observed at 6.5V, 14.0V and 18V respectively. It can be noticed that the Ag and Ti samples with lower barrier heights will have light emissions at lower voltages, in which two Schottky contacts were probed as cathode and anode. However, the lowest barrier height does not mean that the sample will be able to start emitting light at the lowest voltage. The ability to emit light at low bias may depend on the type of metal used for Schottky contacts fabrication.

Under increasing bias, the blue-shifting electroluminescence spectra evolved from longer wavelength involving deep level states to shorter wavelength involving shallow acceptor levels was found. Therefore, the change of emission colour from yellowish white, green, blue to violet could be observed when the potential between the electrodes was increased gradually. The light emitted would be saturated for higher bias (>25V) due to inherent joule heating as high current was injected into the device, eventually the metal contact would be damaged and burnt.

The electroluminescence produced by Ag1, Ag2, Ti1 and Ti2 could be attributed to the electrons injected from the metal contact under a forward bias into p region created by Mg doping and recombined with holes from different emission centres which lead to different emission colours.

Column II dopants or impurities, i.e. Mg can either substitute for Ga to form single acceptors or substitute for N to form deeper triple acceptors. Since *a priori* the acceptor can occupy both sites, Mg should be a quadrupole acceptor, which forms four different levels above the valence band [10]. Apart from these levels, there are other deep acceptors, which involve defects associated with Mg doping [11]

The yellow emission, a broad band centred at ~2.2 eV which is normally observed in undoped and n-type GaN is interpreted as a transition from a shallow donor to a deep acceptor located at about 1 eV above the valence band [12,13], however, based on first principles calculations, Neugebaur and Van de Walle suggest that the yellow emission could be related to a deep level generated by a complex defect involving Ga vacancies, whose formation energy increases in p-type GaN with higher Mg doping concentration [14, 15].

The green emission, increases in intensity and blue-shift to higher energy when applied bias is increased. This recombination involves deep emission centres. Since these ELDs experience a large shift, the transition does not behave as a donor-acceptor pair (DAP) recombination, it indicates that the defects are located in a broad, multi-level band. The energy shift from yellow to green emission is probably due to the saturation of the lowest energy levels; either they behave as deep donor or as deep acceptors [11].

The origin of blue and violet emissions could be related to the energy level introduced by Mg doping and defects in GaN. Deep donors associated to nitrogen vacancies in p-GaN, V_{N3+}, which forms at a level 0.9 eV above the valence band , and a level related to Mg doping V_{N-Mg2+}, at 0.7 eV above the valence band [16], in addition, the hydrogenated nitrogen vacancies, V_{N-H} also could be involved in the blue-violet emission [17].

4. Conclusion

Nickel ohmic contacts and Schottky contacts using silver or titanium were fabricated on Mg-doped p-GaN films. Different light emission colours have been observed from these thin film electroluminescent devices. Lower barrier heights were obtained for samples with both Schottky contacts probed as cathode and anode as compared to the samples where Schottky and ohmic contacts used as cathode and anode. Contacts of Ag and Ti with lower barrier heights were found to have light emissions at lower voltages. The ability to emit light at low applied bias could be dependent on the type of metal used for Schottky contacts fabrication.

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Figure captions

Figure 1. (a) Top view, and (b) cross section view of ohmic and Schottky contacts of a typical sample

Figure 2. The I-V characteristics of the samples with Schottky contacts made of (a) silver and, (b) titanium; under three different probing conditions

Set of Figures

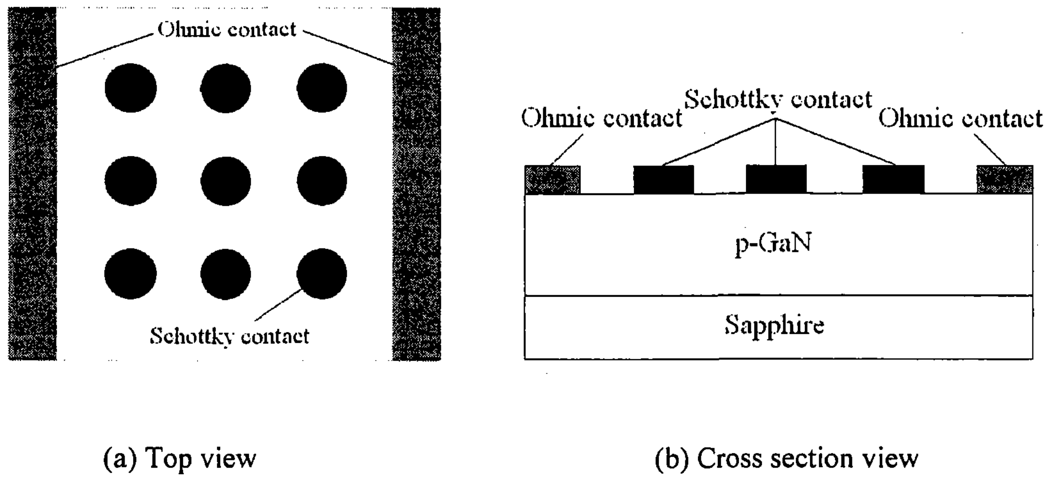
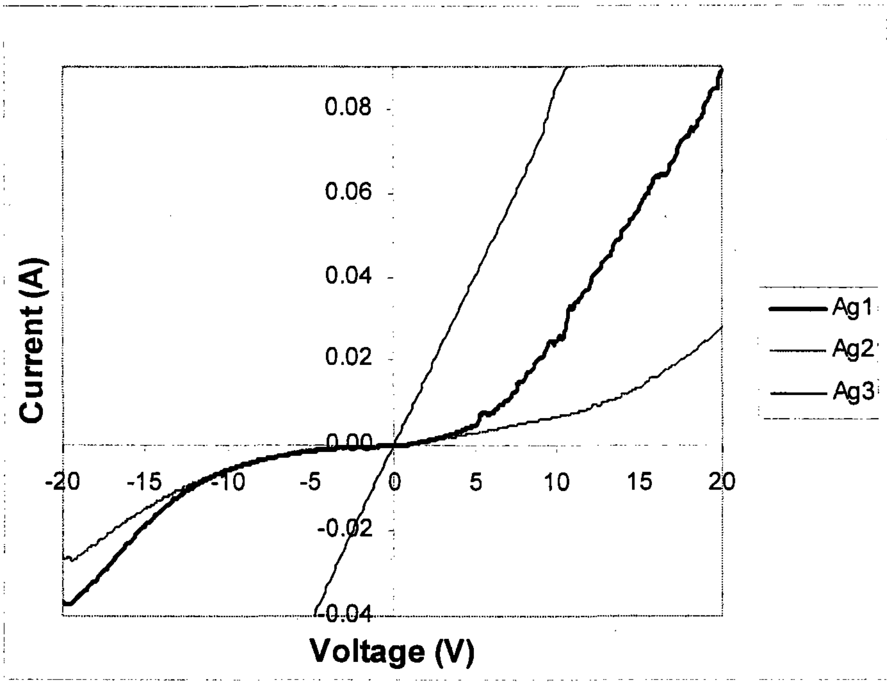
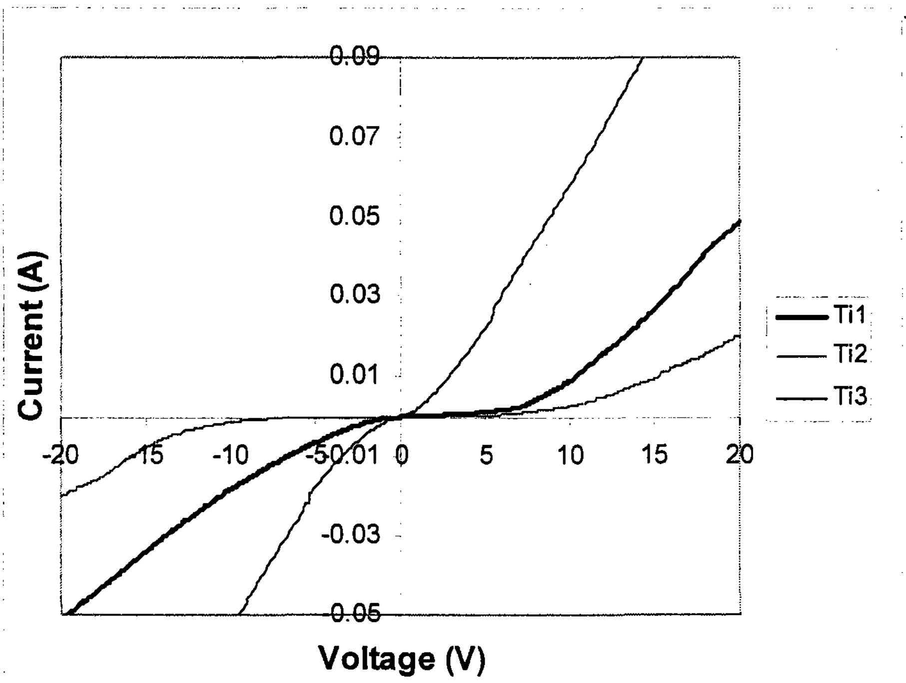


Figure 1. (a) Top view, and (b) cross section view of ohmic and Schottky contacts of a typical sample



(a)



(b)

Figure 2. The I-V characteristics of the samples with Schottky contacts made of (a) silver and, (b) titanium; under three different probing conditions.

27287

Dark Current Characteristics of Thermally Treated Contacts on GaN-based Ultraviolet Photodetectors

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Keywords: Photodetectors, III-V nitrides, Cryogenic, Metal-Semiconductor-Metal (MSM) Photodiodes, Thermal Annealing.

Abstract

The III-V nitrides (GaN and AlGaN) are being actively investigated recently for its potential as ultraviolet (UV) photodetector materials. One of the most important considerations in fabricating a photodetector is achieving a low dark current condition, which is critical in producing UV photodetectors with a high signal-to-noise ratio. For this purpose, thermal treatment has been proven to be a useful method in reducing the leakage current in a Schottky contact, as well as reducing the dark current in a Schottky contact based metal-semiconductor-metal (MSM) photodetector. In this work, GaN based MSM photodetectors (photodiodes) with nickel (Ni) Schottky contacts were fabricated and characterized. The application of thermal treatment to the contacts at various annealing temperatures (400°C-700°C) was investigated. Cryogenic cooling after heat treatment was also performed to determine the effects of this treatment on the electrical characteristics of the devices. Electrical and morphological characterization was performed by current-voltage (I-V) and atomic force microscopy (AFM) measurements respectively.

1. Introduction

The research on wide band gap semiconductors such as the III-V nitrides, AlGaN, and SiC has led to many advances in the field of optoelectronics. In recent years, the GaN and AlGaN are being actively investigated for its potential in ultraviolet (UV) photodetection such as flame sensing, missile plume detection, UV biological effects, UV astronomy, engine control, and secure space-to-space communications. The many advantages for fabricating optoelectronic devices based on the wide band gap semiconductors mentioned above are due to the outstanding thermal and chemical stability which enable them to operate at high temperatures, high powers and also in hostile environments.

One of the most important considerations in fabricating a photodetector is achieving a low dark current condition, which is critical in producing ultraviolet (UV) photodetectors with a high signal-to-noise ratio. The introduction of the effects of thermal annealing on UV photodetectors based on GaN are investigated, which are mainly due to the high thermal stability of GaN that has prompted us to bring out the best from thermal treatment to the electrical characteristics of the UV photodetectors. Thermal treatment has been proven to be useful in reducing the leakage current in Schottky diodes, as well as reducing the dark current in a Schottky contact based metal-semiconductor-metal (MSM) photodetector [1,2] which is the subject that we are discussing in this paper.

2. Experimental

The GaN (grown on sapphire (Al_2O_3) substrate) samples used for the fabrication of the photodetectors are transparent, with a thickness of about 4.5 μm, are unintentionally doped n-type, and have a background electron concentration in the high $10^{16}cm^{-3}$ range. Our photodetectors are the metal-semiconductor-metal (MSM) photodiodes with both interdigitated contacts (electrodes) forming Schottky barriers. The fingers width is 230 μm and the finger spacing is 400 μm. The length of each electrode is about 3.3 mm, and it consists of 4 fingers at each electrode.

The metal that was used for forming both interdigitated Schottky contact electrode was thermally evaporated. For the wafer cleaning process prior to metallization of the contact metal, the GaN samples were dipped in a 1:20 $NH_4OH:H_2O$ solution for 15 seconds followed by a 10 seconds dip in a 1:50 $HF:H_2O$ solution. The last step of the cleaning process was a 10 minutes etch in boiling aqua regia ($HCl:HNO_3$ = 3:1). The fabricated photodiodes were then annealed at temperatures from 400°C-700°C in a conventional tube furnace in flowing nitrogen environment. For the samples (photodiodes) annealed at temperatures from 400°C and 500°C, the annealing duration was 15 minutes, while the 600°C samples were annealed for 5 minutes and 2 minutes for the 700°C samples. Samples were prepared in pairs for each annealing temperature. The objective was just to study the annealing effects (*A*) and also cryogenic cooling effects right after annealing treatment (*A*+*C*) to the photodiodes' performance following some encouraging results reported for this kind of low temperature treatment to ohmic contacts [3]. Therefore, apart from studying the effects of annealing treatment to the photodiodes, the effects of cryogenic treatment were studied where some of the samples were subsequently cooled in liquid nitrogen right after annealing treatment.

The electrical properties of the photodiodes were analyzed by means of I-V characteristics of the devices. Atomic force microscopy (AFM) was used to analyze the morphological properties of the samples.

3. Results and Discussions

The Schottky contact properties of the MSM photodiodes can be closely described by the equation below [4,5]

$$I = I_0 \exp(\frac{eV}{nkT})[1 - \exp(\frac{-eV}{kT})] \quad (1)$$

where I is the current, I_0 is the saturation current, V is the bias voltage, and n is the ideality factor. The expression for the saturation current, I_0 is

$$I_0 = SA^* T^2 \exp(\frac{-e\Phi_b}{kT}) \quad (2)$$

where S is the Schottky contact area, Φ_b is the Schottky barrier height, and A^* is the Richardson constant where here we use the theoretical value of A^* [6] to be 26.4 $Acm^{-2}K^{-2}$. Equation (1) can be rewritten as

$$\frac{I \exp(eV / kT)}{\exp(eV / kT) - 1} = I_0 \exp(eV / nkT) \quad (3)$$

At $T \leq 370K$ and when $V \leq -0.5V$, equation (3) can be simplified to

$$I \exp(\frac{eV}{kT}) = I_0 \exp(\frac{eV}{nkT}) \quad (4)$$

$$\ln [I \exp(\frac{eV}{kT})] = \ln I_0 + \frac{eV}{nkT} \qquad (5)$$

Here, the plot of $\ln [I \exp(eV / kT)]$ vs V will give a straight line with the slope = e/nkT and y-intercept at $\ln I_0$.

By referring to Table 1, we found that high temperature annealing (600°C and 700°C) resulted in a more significant changes to the dark current characteristics compared to the lower temperature annealing treatment. High temperature annealing treatment increased the barrier height as well as reduced the dark current level, and also with a stable ideality factor when compared to the as-deposited conditions. For lower temperature annealing (400°C and 500°C), the barrier height for the *A+C* treated samples increased while the *A* treated samples experienced a reduction in the barrier height. This is mainly due to the better surface morphology of the *A+C* treated samples. This phenomenon will be discussed later in this paper. However, under high voltage stressing at 15V, all of the samples experienced an increase in dark current level except for those samples annealed at 600°C and 700°C upon comparison with their respective as-deposited samples. A 45% reduction in dark current level is observed (Fig. 1) in the 700°C samples while the 600°C samples experienced a 31% reduction in dark current level (Fig. 2) at 15V. Thus, here we can see that high temperature annealing is more significant in producing a more stable and preferable electrical characteristics of our MSM photodiodes because the samples treated under high temperature resulted in not only an increase in the Schottky barrier height, but are also able to withstand high voltage stressing i.e. the dark current level has reduced when compared to the as-deposited condition at 15V biasing. Other than that, the high dark current level and low barrier height of the photodiodes are mainly due to high tunneling component resulting from high background carrier concentration, defects present in the films, and also due to the fact that MSM photodiodes are being operated at reverse bias mode where the effect of applied bias can be much greater when compared to the forward bias mode of a normal Schottky diode.

Due to degradation of the metal contacts of the samples under A treatment at temperatures of 600°C and 700°C, we could not obtain any data from the I-V measurement system. However, the application of cryogenic treatment does help in preventing severe degradation of the metal contacts under high temperature annealing. We suspect the diffusion of Ni metal layer into the samples away from the GaN surface has resulted in a degraded metal-semiconductor contact for the samples under A treatment. Since the samples were still hot at the time they were taken out of the furnace, a great deal of diffusion of the metal layer will still take place. Thus here, the effect of cryogenic cooling right after thermal annealing in this case will minimize the diffusion of the metal layer which then led to a better metal-semiconductor contact. In fact $A+C$ treatment has led to achieving a smooth surface morphology of the metal contacts of the photodiodes as confirmed by our AFM data. All of the samples under $A+C$ treatment have a smaller root mean square (rms) surface roughness than the annealed-only (A) samples, indicating a better (smoother) surface morphology. For the $A+C$ treated samples, the smallest rms value came from the 400°C samples which has a value of 1.25 nm (Fig. 3), followed by the 600°C (Fig. 5) and 500°C (Fig. 4) samples with a value of 2.29 nm and 4.06 nm respectively, while the highest rms value came from the 700°C samples with a value of 9.41nm (Fig. 6). The smoother surface morphology of the $A+C$ treated samples which resulted in better electrical properties can be attributed to the subsequent and fast cooling of cryogenic treatment which minimizes the effect of compressive stress and strain induced in the metal-semiconductor contact resulting from the heating and cooling process of normal annealing treatment [3]. The compressive stress and strain present during the heating process as well as the cooling down process to room temperature after annealing can be attributed to the differences of thermal expansion coefficient between the Ni ($\alpha \sim 13.4\times10^{-6}$ K^{-1}) [11] and GaN ($\alpha \sim 6\times10^{-6}$ K^{-1}) [12]. Thus, *A+C* treatment has resulted in a laterally more uniform contact surface which is essential for achieving a metal-semiconductor contact with good electrical properties.

4. Conclusion

The application of thermal annealing treatment to our Ni/GaN MSM photodiodes at various annealing temperatures (400°C-700°C) was investigated. Significant improvement to the Schottky contact properties of the photodiodes which resulted in the reduction of dark current level can be achieved at high annealing temperature (600°C and 700°C) with the assistance of cryogenic treatment. High temperature annealing treatment leads to the degradation of the metal-semiconductor contacts of the photodiodes. Smoother surface morphology of the photodiodes' metal contact was achieved after they were annealed and cryogenically cooled. In conclusion, cryogenic treatment after annealing does helps in the enhancement of the electrical and morphological properties of the metal contacts of the photodiodes especially at high temperature thermal treatment.

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Figure captions

Figure 1 Current-voltage (I-V) characteristics of the samples annealed at 700°C

Figure 2 Current-voltage (I-V) characteristics of the samples annealed at 600°C

Figure.3 Atomic force microscopy image of the Ni Schottky contact on the MSM photodiode under $A+C$ treament at 400°C.

Figure. 4 Atomic force microscopy image of the Ni Schottky contact on the MSM photodiode under $A+C$ treament at 500°C.

Figure. 5 Atomic force microscopy image of the Ni Schottky contact on the MSM photodiode under $A+C$ treament at 600°C.

Figure. 6 Atomic force microscopy image of the Ni Schottky contact on the MSM photodiode under $A+C$ treament at 700°C.

Table captions

Table 1: Summary of the dark current characteristics of the samples annealed at different temperatures.

Set of Figures

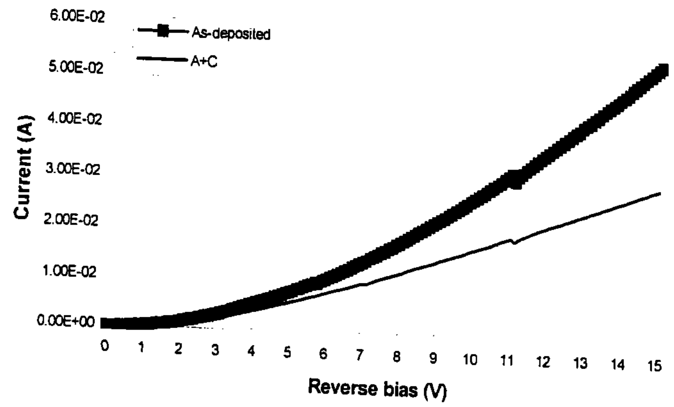

Fig.1 Current-voltage (I-V) characteristics of the samples annealed at 700°C

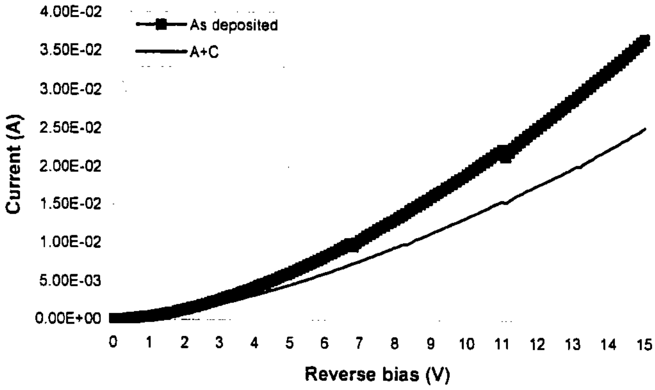

Fig.2 Current-voltage (I-V) characteristics of the samples annealed at 600°C

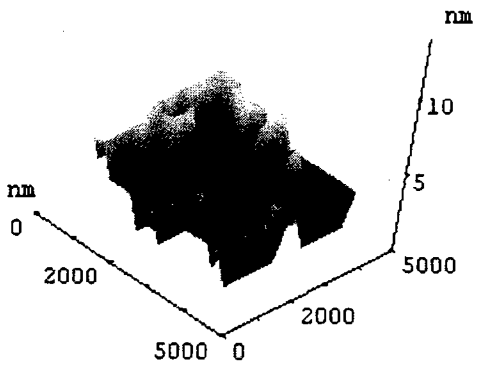

Fig. 3 Atomic force microscopy image of the Ni Schottky contact on the MSM photodiode under $A+C$ treament at 400°C.

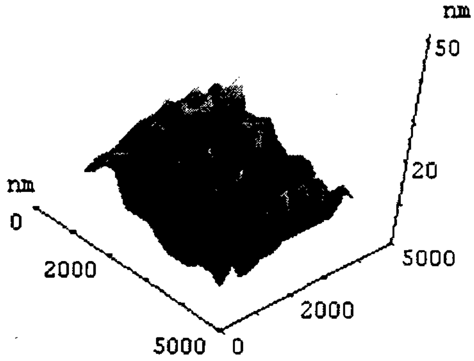

Fig. 4 Atomic force microscopy image of the Ni Schottky contact on the MSM photodiode under $A+C$ treament at 500°C.

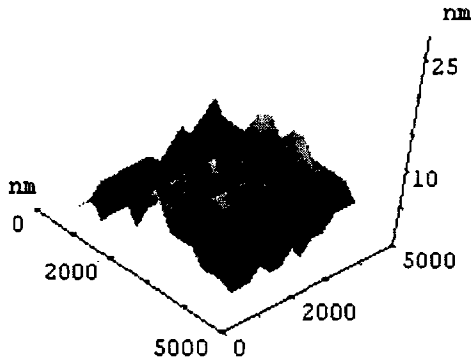

Fig. 5 Atomic force microscopy image of the Ni Schottky contact on the MSM photodiode under $A+C$ treament at 600°C.

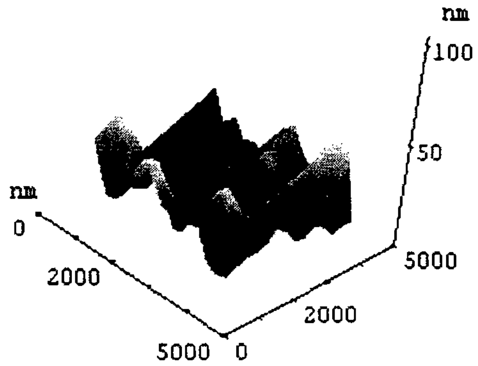

Fig. 6 Atomic force microscopy image of the Ni Schottky contact on the MSM photodiode under $A+C$ treament at 700°C.

Set of Table(s)

Table 1: Summary of the dark current characteristics of the samples annealed at different temperatures.

Temperature (°C)	Samples (MSM photodiodes)	Ideality factor, n	Barrier height, Φ_b (eV)	Current at 15V (mA)
400°C	As-deposited (*A*)*	1.007	0.485	25.0
	A	1.007	0.450	79.3
	As-deposited (*A+C*)*	1.007	0.484	20.3
	A+C	1.010	0.519	29.3
500°C	As-deposited (*A*)*	1.010	0.521	26.9
	A	1.007	0.468	43.3
	As-deposited (*A+C*)*	1.008	0.504	18.5
	A+C	1.009	0.514	20.1
600°C	As-deposited (*A+C*)*	1.007	0.479	36.6
	A+C	1.007	0.488	25.2
700°C	As-deposited (*A+C*)*	1.008	0.480	54.1
	A+C	1.008	0.487	29.7

* Here, we cannot assume that the electrical characteristics of all our samples used to fabricate the detectors are totally identical, as can be seen by the as-deposited Schottky contact properties in Table 1. We have also found this to be true because the current conduction magnitude of the as-deposited Schottky contacts on our MSM photodiodes does varies slightly from one sample to the other as similar claims were also previously reported [7-10]

Note: 1) As-deposited (*A*) : As-deposited samples before annealing treatment.

2) *A* : Samples treated with annealing only.

3) As-deposited (*A+C*) : As-deposited samples before annealing-and-cryogenically-treated.

4) *A+C* : Annealed-and-cryogenically-treated samples.

27286

Barrier Height Enhancement of AlGaN Schottky Diodes

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Keywords: Schottky diodes, III-V nitrides, AlGaN, Cryogenic, Thermal Annealing.

Abstract

The investigation on the Schottky barrier characteristics on AlGaN is of great importance for the high power, high temperature, and high frequency electronic device design. Therefore, it is essential to develop metal contacts which are able to form high Schottky barrier height and superior metallurgical stability in order to produce reliable, efficient, and high performance devices. The application of thermal treatment of Schottky contacts is essential for the enhancement of the Schottky barrier height, which led to smaller leakage current and higher breakdown voltage, and hence the improvement of the the device's noise level and the high voltage performance of the device. Moreover, thermally stable metal-semiconductor contacts are of great importance for high quality devices. In this work, we report on the Schottky contact characteristics of Ni on unintentionally doped n-type $Al_{0.03}Ga_{0.97}N$ grown on sapphire substrates as a function of annealing temperatures (300 to 700°C) with and without the additional application of cryogenic cooling after heat treatment. The Schottky diodes were then analyzed by means of current-voltage (I-V) measurements, atomic force microscopy (AFM), and energy dispersive x-ray analysis (EDX) to study the contact properties of the diodes under annealing-only treatment *(A)* and annealed-and-cryogenically-cooled treatment *(A+C)*.

1. Introduction

The research on III-V nitrides and related materials such as GaN and AlGaN have been actively carried out recently for its remarkable properties like wide and direct band gap, high breakdown electric field, high thermochemical stability, and high electron saturation velocity [1]. Thus, these wide band gap semiconductors are excellent for applications in high power and high temperature optoelectronic as well as electronic devices ranging from blue and green light emitter [1,2], solar-blind UV photodetectors [3-5] to high electron mobility transistors (HEMTs) [6-8]. The wide device applications possibilities of these materials have to be supported by reliable metal-semiconductor contacts in order to ensure a good device performance. For example, a good Schottky contact formation is essential for fabricating a high performance GaN-based Schottky contact-based UV photodetectors [3], or field effect transistors (FET) [8]. For device design, the Schottky barrier height of a metal on a semiconductor is an important parameter, where a high barrier height leads to small leakage currents and high breakdown voltages [9] which will result in improvement of the device's noise level [10] and its high voltage performance. Studies have reported that the effects of thermal annealing will lead to an enhancement in the barrier height of a Schottky contact [11-13]. However, the quality of some metal-semiconductor contact will degrade upon high temperature annealing, owing to the deterioration of surface morphology and chemical reactions. Therefore, the introduction of cryogenic treatment right after thermal annealing of Schottky contacts is investigated for its role in improving the contacts morphological characteristics as well as its electrical properties. There were also encouraging results about cryogenic treatment in improving GaN-based ohmic contacts [14]. As the introduction of cryogenic treatment to metal-semiconductor contacts or device processing is still very rarely reported, more work has to be done to find out its importance.

Thus in our present work, we have investigated the thermal annealing effects as well as the thermal stability of Ni-$Al_{0.03}Ga_{0.97}N$ Schottky diodes at a range of annealing temperatures. In order to study the effects of cryogenic cooling, the Schottky diodes were subsequently dipped into liquid nitrogen right after thermal annealing.

2. Experimental

Our AlGaN samples used for this study have a 3 % aluminium (Al) mole fraction or better known as $Al_{0.03}Ga_{0.97}N$, and were unintentionally doped n-type and grown on sapphire substrates. The AlGaN samples have an active layer thickness of 0.5 μm. Prior to contact metallization, the AlGaN samples were firstly cleaned in a 1:20 $NH_4OH:H_2O$ solution for 15 seconds followed by a 10 seconds dip in a 1:50 $HF:H_2O$ solution. Finally, the samples were etched in boiling aqua regia ($HCl:HNO_3$ = 3:1) for 10 minutes and then cleaned in deionized water before they were brought into the evaporator system. A metal mask was used in the patterning of the Ni Schottky contact structure (Ni dots) which was positioned at the center of the samples while the ohmic contacts were two silver (Ag) metal stripes positioned on the sides of the samples. The Ni dots each has a diameter of about 250 μm. The as-deposited silver metal contacts were ohmic as confirmed by I-V measurement. The samples (Schottky diodes) were then annealed at a range of temperatures starting from 300°C to 700°C in flowing nitrogen by using a tube furnace. The annealing duration for the samples annealed at temperatures from 300°C to 500°C was 15 minutes, while the 600°C samples were annealed for 5 minutes and 2 minutes for minutes for the 700°C samples. In the study of the effects of cryogenic cooling, samples were prepared in pairs for each annealing temperature. One of the diodes in each annealing temperature will be cooled in liquid nitrogen immediately right after it was taken out from the furnace while the other will be left to cool down to room temperature.

The Schottky diodes were then analyzed by means of current-voltage (I-V) measurements, atomic force microscopy (AFM), and energy dispersive x-ray analysis (EDX) to study the contact properties of the diodes under annealing-only treatment *(A)* and annealed-and-cryogenically-cooled treatment *(A+C)*.

3. Results and Discussions

The I-V characteristics of the Schottky diodes were determined by assuming thermionic emission. For V>3kT/q, the general diode equations are

$$I = I_0 \exp(qV/nkT) \tag{1}$$

where I_0 is the saturation current and is written as

$$I_0 = SA^*T^2 \exp(-q\Phi_B/kT) \tag{2}$$

By referring to equation (1) and (2), q is the electronic charge, V is the applied voltage, n is the ideality factor, k is the Boltzmann constant, T is the absolute temperature, S is the contact area, A^* is the effective Richardson constant, and Φ_B is the Schottky barrier height. Here the value of A^* for $Al_{0.03}Ga_{0.97}N$ was estimated to be 27.2 $Acm^{-2}K^{-2}$ and it should be noted that a large variation in A^* does not have a significant influence on the Φ_B value that is to be determined [15]. The plot of *ln I* vs *V* will give a straight line with a slope of q/nkT with the y axis intercept at $ln\ I_0$ where the barrier height, Φ_B can be determined according to equation (2).

As shown in Fig.1, all the annealed Schottky diodes showed an enhancement of barrier heights when compared to the as-deposited sample with the exception of the samples under the 600°C annealing condition. This may be due to macroscopic interactions between the contact metal (Ni) and the active layer (AlGaN) where under this temperature, the Ga appeared to have migrated into the Ni contact metal on top [15] i.e. the chemical reaction that occurred under this high temperature had led to a new phase formation (Ni-Ga solid solution) [16] where these chemical reaction may be the main cause of barrier lowering. This phenomena does not seems to affect the 700°C samples treated with cryogenic cooling. This may be due to firstly, the brief annealing time (2 minutes) being introduced to the sample and secondly, the fact that the effect of cryogenic cooling prevents the advancement of the chemical reactions which occur faster at high temperatures as compared to the annealed only sample where it was left to cool down to room temperature after it was taken out from the furnace. The annealed sample at such a high temperature is still hot and the phenomena as described above can still happens. However, at such a temperature, the Schottky diode characteristics under the annealed-only treatment at 700°C has deteriorated, which yielded a root mean square (RMS) surface roughness of 31.72 nm by our AFM measurement which confirmed the degraded state of the diode's contact structure. Hence no data was obtained from the 700°C annealed-only condition.

From the calculated barrier height as shown in Table 1, most of the samples have a higher barrier height under *A+C* treatment which may be due to smoother surface morphology of the contacts (as confirmed by our AFM measurements) as a good uniform surface morphology is a key to achieving a better contact with good electrical characteristics. The smoother surface morphology may be attributed to the subsequent and fast cooling of cryogenic treatment which minimizes the effect of compressive stress and strain induced in the metal-semiconductor contact resulted from the heating and cooling process of normal annealing treatment [14]. The compressive stress and strain present during the heating process as well as the cooling down process to room temperature after annealing can be attributed to the differences of thermal expansion coefficient between the contact metal and the active layer of the semiconductor [14]. The only exception came from the 300°C samples where the calculated barrier height for the *A+C* treated sample is slightly lower than the annealed-only sample. Moreover, the *A+C* treated samples also has a larger reverse leakage current which is unexpected. As reported, most Ni-GaN based contacts are expected to be stable at an annealing temperature of below 600°C without any sign of macroscopic interactions as described above [12,15,16]. Therefore the two discrepancies as described above may be due to some variations in defect densities and contamination level caused by sample preparation between the two 300°C samples.

The optimum condition came from the 400°C (*A+C*) sample (Fig. 2) with the highest barrier height obtained (1.01eV) and the lowest leakage current 1.12×10^{-8} A at -8V. The 500°C (*A+C*) sample also came close with a barrier height of 0.97eV and a leakage current of 9.35×10^{-7} A. These optimum conditions of barrier height enhancement may be attributed to intimate contact formation between the contact metal and the semiconductor. In normal sample processing method, Schottky diodes nearly always have a thin interfacial layer between the metal and semiconductor unless they are manufactured by cleaving the semiconductor in an ultra-high vacuum environment, and the existence of this interfacial layer is responsible for the lower barrier height of the as-deposited contacts [17]. Thus, upon annealing, the Ni metal layer is expected to diffuse into the contamination layer and grow epitaxially on the GaN surface without forming a new intermixing layer at the GaN/Ni interface [18]. Therefore the two discrepancies of the 300°C samples as described earlier where the lower barrier height and higher reverse leakage current obtained from the $A+C$ treatment may be due to the immediate halt to the Ni diffusion through the interfacial layer by cryogenic cooling which resulted in a less-intimate contact as interdiffusion process is slower at lower temperatures. The case is different for the 300°C sample as it was left to cool down to room temperature by itself without exaggerated fast cooling like the $A+C$ treatment. Therefore, the Ni diffusion process (through the interfacial layer) may be still happening, and thus resulted in a better contact when compared to the $A+C$ treated sample. Thus, in order to achieve a satisfactory intimate contact, we recommend a longer annealing duration (>15minutes) for the 300°C treatment. Therefore, for an annealing duration of not less than 15 minutes, we may conclude that 400°C is the threshold annealing temperature for producing an intimate metal-semiconductor contact for our Ni-AlGaN Schottky diodes where the further limitation for the achievement of good Schottky contact properties above 400°C are the surface uniformity and chemical reactions of the contacts.

The diodes at higher annealing temperatures (600°C and 700°C) exhibit a large amount of leakage current comparable to the as-deposited diode's leakage current, where this behaviour can mainly be attributed to the effects of macroscopic interactions as described earlier and the release of nitrogen (N) to the environment upon high temperature annealing [16,19]. The release of N out from the AlGaN surface causes nitrogen vacancies which is commonly thought to increase the background electron concentration in AlGaN or GaN films. Thus, the high surface carrier concentration might increase the tunneling at the metal/n-AlGaN interface under the reverse bias for the Schottky diodes, which resulted in the increase of the reverse leakage current [19]. The loss of nitrogen from the AlGaN surface has been confirmed by the EDX measurements for all the samples except the 600°C (*A*) sample where there was still a significant amount of N present in the AlGaN film. The inconsistency for the 600°C samples is still under investigation.

4. Conclusion

From our results, it is seen that annealing does enhance the Schottky barrier height, Φ_B of the as-deposited Ni/n-$Al_{0.03}Ga_{0.97}N$ Schottky contact and further enhancement is achieved by the application of cryogenic treatment. The advantage of cryogenic treatment is mainly due to the improvement of the surface morphology of the Schottky contacts. The achievement of a good Schottky contact properties will require an intimate metal-semiconductor contact and a uniform surface morphology. The optimum condition came from the 400°C (*A*+*C*) sample with the highest barrier height of 1.01eV and the lowest leakage current of 1.12×10^{-8} A at -8V. For an annealing duration of not less than 15 minutes, 400°C is the threshold annealing temperature for producing an intimate metal-semiconductor contact for our Ni/n-$Al_{0.03}Ga_{0.97}N$ Schottky diodes where the further limitation for the achievement of good Schottky contact properties above 400°C are the surface uniformity and chemical reactions of the contacts. Prolonged annealing at higher temperatures (600°C and 700°C) will lead to deterioration of the Schottky contact properties.

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Figure captions

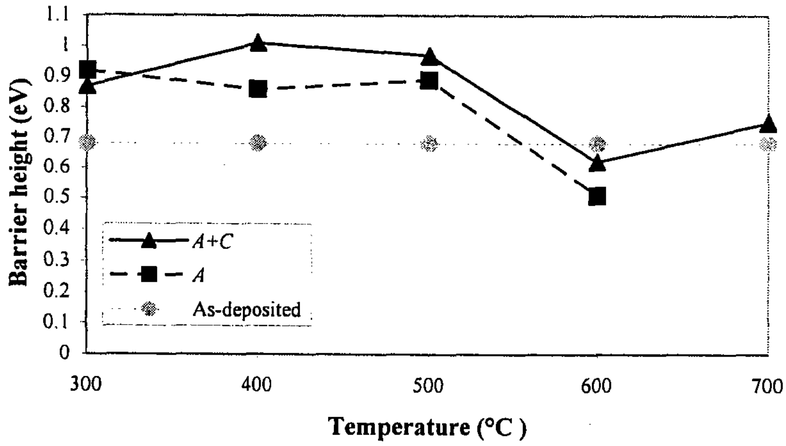
Figure 1 Change in the Schottky barrier height, Φ_B as a function of annealing temperature.

Figure 2 A comparison of the diode's I-V characteristics at optimum annealing condition (400°C) with the as-deposited condition.

Table captions

Table 1 Summary of characteristics of the AlGaN Schottky diodes annealed at different temperatures.

Set of Figures



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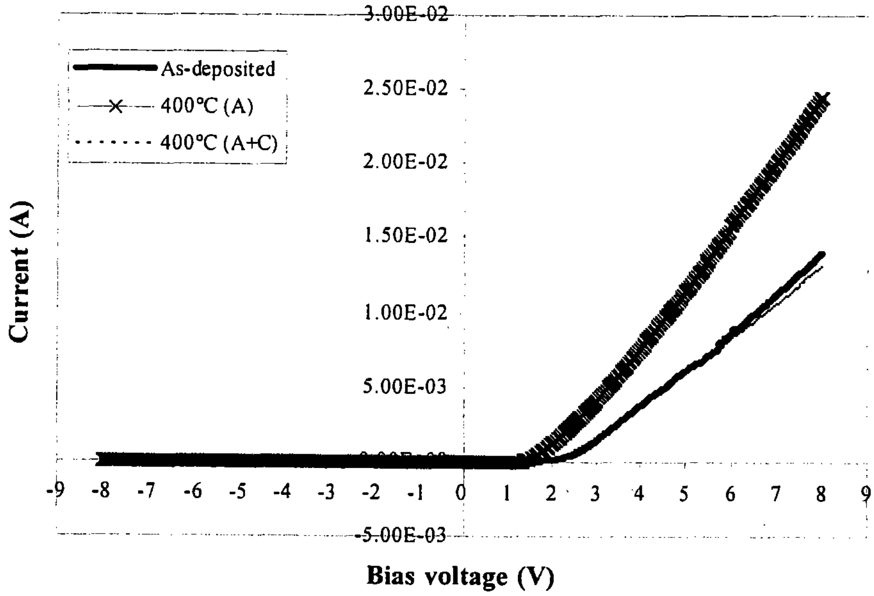

Fig. 2 A comparison of the diode's I-V characteristics at optimum annealing condition (400°C) with the as-deposited condition.

Set of Table(s)

Table 1 Summary of characteristics of the AlGaN Schottky diodes annealed at different temperatures.

Condition	Barrier height, Φ_B (eV)	Reverse leakage current at 8V (A)	Root mean square (RMS) surface roughness (nm)
As-deposited	0.68	4.22×10^{-5}	2.89
300°C (*A*)	0.92	2.84×10^{-7}	4.80
300°C (*A+C*)	0.87	1.18×10^{-6}	4.58
400°C (*A*)	0.86	6.12×10^{-7}	5.97
400°C (*A+C*)	1.01	1.12×10^{-8}	4.39
500°C (*A*)	0.89	8.08×10^{-7}	7.28
500°C (*A+C*)	0.97	9.35×10^{-7}	6.42
600°C (*A*)	0.51	1.05×10^{-4}	5.07
600°C (*A+C*)	0.62	6.01×10^{-5}	4.57
700°C (*A*)	*	*	31.72
700°C (*A+C*)	0.75	1.21×10^{-5}	4.10

* The diode's characteristics deteriorated under this condition.