Progress in the fabrication of GaN Photo-Cathodes

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ABSTRACT

Currently, photo-cathodes hold the highest promise in the near term (next few years) of being able to detect low light level UV signals at high QE while being nearly blind to visible wavelengths. We briefly discuss the requirements for UV detection for astronomical applications, and then we describe our work on producing GaN based photo-cathodes. The p-type GaN films were grown on sapphire at Northwestern University. The films were then converted into opaque photo-cathodes inside photo-tubes at Hamamatsu. Hamamatsu tested detective quantum efficiencies (DQE) of these detectors to be as high as 30% at 200 nm. The ratio of peak DQE at 200 nm to the minimum DQE at 500 nm was measured to be about 6×10^3. We found a dramatic increase in the DQE at 200 nm versus the conductivity, with the break point being near 0.13 1/(Ohm-cm). Based on this dramatic increase, we believe that further improvement in photo-cathode quantum efficiencies can be achieved by increasing the conductivity. We have recently achieved more than an order of magnitude increase in conductivity by co-doping techniques. Improvements in the solar blindness of the devices depend both on characteristics of the film and its surface properties. A detailed discussion of decreasing the visible response and producing a sharper wave-length cutoff is beyond the scope of this work, but we briefly discuss the attributes that most likely affect the wavelength dependence of the photo-cathode response.

Keywords: UV, visible-blind, photo-cathode, co-doping

1. INTRODUCTION

1.1. General Comments

The desire to make detectors that are visible-blind and highly quantum efficient in the UV is driven by applications for astronomy, industry, and the military. The needs of the astronomical community have been detailed in the past,[1–4] and a discussion of a wider range of applications can be found elsewhere.[5] As here we are describing our work on photo-cathodes, it is worthwhile to emphasize and review the importance of developing photo-cathodes for astronomy, which we do in the next subsection.

1.2. UV Astronomy and the Importance of Photo-Cathodes

There are two basic criteria for UV astronomy: (1) the ability for photon-counting; and, (2) high (40% or more) detective quantum efficiency (DQE) above a selected energy ($\sim 3.0 - 6.0$ eV) to less than 10^{-6} (and, if possible, we would like this to be as low as 10^{-8}). The faint light level requirement is because even with telescopes, the typical flux levels with stars and galaxies in the UV is less than one photon/pixel-sec (and in comparison, the tests in the literature typically use 10^{11} photons/pixel-sec.) The need for a sharp cut off in efficiency is driven by the flux distribution which can be as much as 10^8 times higher in the visible ($\sim 1.5 - 2.5$ eV) as in the UV.

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There are other requirements such as the ability to have a large dynamic range in counting rate both locally and over the entire field of the device. These issues have been discussed previously,[1–4,6] and we won't review them again here. There are, however, two issues in comparison with solid state detector that deserve further discussion.

These are the issues of dark current and responsivity. Although GaN-based solid state devices have made great strides in recent years (see for example, reference 7) and some devices have given DQE values over 80% (Joseph, private communication), the dark currents are still a factor of at least 10^5 higher than for Si CCDs. However, these p-i-n diodes have no gain, and to our knowledge, readout systems do not yet exist to store and amplify single photon events, i.e. these p-i-n diodes must be illuminated by sources that are many times brighter than stars (even enhanced with a telescope). Eventually we expect that, if the commercial applications are numerous, GaN-based CCD-like devices will be developed.

Regardless of CCD-like device development, when large detector areas (square meters) are required, the CCD devices fall short as the costs of covering such large areas become prohibitive. Two experiments that need these large areas are OWL[8] (337 nm, 360 nm, and 391 nm for nitrogen fluorescence lines) and Çerenkov light (about 400 nm and shorter) gamma-ray observatories such as VERITAS.[9] The former needs about million 2.5 mm ×2.5 mm pixels and the later about 1000 about 2.5 cm × 2.5 cm pixels. The later needs to be blind long-ward of ∼ 400 nm to block out most of the background and still be sensitive to the Çerenkov radiation. GaN has an advantage over diamond in that GaN is "tunable" by alloying it with aluminum to move the band gap to higher energies and with indium to lower energies.[10]

One of the major hurdles to overcome in fabricating these photo-cathodes is that the films must be p-type. This is because of the requirement for surface band-bending, which lowers the work function sufficiently so as to make an effective photo-cathode. Making p-type films with high carrier concentrations and high carrier mobility is required (as we demonstrate below), but this is difficult to achieve.

2. GAN FILM FABRICATION: THEORY AND PRACTICE

2.1. Theory

The most effective dopant p-type carrier is Mg, but it has a high ionization energy of about 200 meV. The relatively high ionization energy leads to on the order of one percent ionization at 300K so that 100 times the element concentration is needed to achieve a given hole density. For the specific case of Mg, a goal of 2×10^{18} cm^{-3} near room temperature (300K) leads to a requirement of about 2×10^{20} cm^{-3}, but this 2×10^{20} cm^{-3} value is near the solubility limit for Mg. Such high impurity concentrations produce relatively high resistivity and low hole-mobility, which is exactly the opposite of what we desire, i.e. as we show below, we would like low resistivity.

We describe in the next subsection how improved carrier concentration and resistivity can be achieved by co-doping the Mg with H, O, or Si. There are two processes that may be important[11]: (1) co-doping of GaN should lead to increased solubility due to the formation of donor-acceptor complexes such as O_N-$2Mg_{Ga}Be_{Ga}$, which increases the solubility; (2) an alternative hypothesis is that carrier mobility of the co-doped samples increases due to the replacement of the long-range Coulomb scattering for simple single doping by short-range dipole scattering in co-doped films.

2.2. Increasing the solubility of Mg in GaN

The formation energy E^f of defect of dopant in semiconductor is given by the following equation

$$E^f(q) = E^{tot}(q) - \sum_a n_a \mu_a - qE_F \quad (1)$$

where E^{tot} is the calculated total energy of a defect species, μ is the chemical potential of n number of atoms, q is the charge of the defect, and E_F is the Fermi level. The formation energy of various defects in GaN has been plotted as a function of the Fermi level in the Figure 1. This figure is based upon previous published calculations and plots.[12,13] As the formation energy of a defect decreases, its solubility in the semiconductor increases, and therefore a low formation energy is desirable for dopant species. Mg is a common p-type dopant in GaN. However, as the material becomes more p-type (E_F moves towards the valence band), the formation energy of the substitutional Mg increases, which limits its solubility. In order to increase the solubility of Mg, it can be co-doped with a donor

species like H, O or Si. When both H (or O or Si) and Mg are present, the Fermi level is pinned at the intersection of their curves. At this point, the formation energy of the Mg is lower than the Mg-only case, and as more Mg is incorporated the E_F levels move to lower values (equivalent to increasing p-type carrier concentration). Hydrogen is a very useful co-dopant, since it, in principle, can be removed by thermal annealing in a nitrogen atmosphere. In the case of Mg-O co-doping, the Fermi level is pinned at an even lower formation energy for Mg incorporation, which should lead to even greater Mg incorporation than for H, and by inference, co-doping with Si will be even better.

To achieve a net concentration of p-type acceptors an excess of acceptors over donors is required. For highly doped material only a small deviation from equilibrium is required to lead to a large net acceptor concentration. We have been able to achieve concentrations as large as 10% of 1×10^{19} cm^{-3} = 1×10^{18} cm^{-3} by co-doping Mg with O. In Figure 2 we show the results of the carrier concentrations and mobility as function of O concentration for a fixed concentration of Mg in GaN.

For this particular case, we see that carrier concentration raises relative rapidly until just before the carrier type changes over from p- to n- type. At the same time, for this combination the mobility is also increasing. This is important as we show below the performance of our PTs depends on the conductivity = $p \times e \times \mu$, where p is the carrier concentration, e is the electron charge and μ is the mobility. That the mobility tends to increase with carrier concentration is not always the case, however, as can be seen in Figure 3. More films with optimal values of p and μ need to be made, and more photo-cathodes need to be made as well to converge on an optimal set of parameters for making films and photo-cathodes. Due to time constraints, the results that we show below are not for the optimal values we have most recently produced via co-doping, but the results are still very good. Therefore, with better films such as the new ones we have made via co-doping, we expect to be able to make photo-tubes that will meet the requirements of astronomers, which are in terms of device requirements the most demanding of any photo-tube user group.

In the next section we describe our progress in the area of making p-type GaN and the results of making photo-tubes with these films.

2.3. Fabrication of the Films

The fabrication of films is described in detail elsewhere,[14] but we give a summary here to make this paper more complete. MOVPE was used to grow GaN films on 001 (c-plane) sapphire substrates. The Mg doping source was biscyclopentadienylmagnesium (Cp_2Mg). For O doping a 510-ppm mixture of oxygen in nitrogen with H as the carrier gas was used. Several layers were deposited to produce the final product: (1) an epilayer of 20 nm thick GaN deposited at 600 C; (2) a 1 μm semi-insulating ($> 100\Omega$-cm) GaN:Mg grown at 1060 C; (3) a 0.7 to 1.0 μm of heavily doped Mg. Then for co-doping, this layer was followed by an O-co-doped GaN layer. The samples were then annealed to 950 C for five minutes in nitrogen to activate the Mg acceptors.

In order to measure the electronic properties of the films, Ni/Au contacts (100/50 nm) were deposited via electron beam evaporation, and carrier concentrations were determined by using the van der Pauw Hall effect in which a magnetic field of 0.4 Tesla and currents between 10-50 μm were applied. Figure 2, which was taken from reference 14, shows how for a steady flow of Mg, a variation in the flow of O can produce produce a carrier concentration as high as 2×10^{18} and a resistivity as low as 0.2Ω-cm. We have not had the opportunity to use such high quality films in the fabrication of photo-cathodes, but given the response of the photo-cathodes we have made, we are very encouraged about making photo-cathodes with this material and measuring the response of the resulting devices. For reflection mode or so-called opaque photo-cathodes, the efficiency potentially could be well above 50%. It remains to be seen, though, how the properties of co-doped GaN affects the sharpness of the cut-off of the response below the band-gap energy.

The work with diamond[15] shows that the band-gap energy does (as we would expect) affect the low energy cut-off energy, but the cut off for the diamond photo-cathode was not as sharp as we observed for our best GaN sample. Nevertheless both the diamond and GaN results predict that it will be possible to make commercially viable photo-tubes and micro-channel plates with diamond and GaN-based films.

3. RESULTS

We have made both singly doped and co-doped samples and compared the properties of the films. We have not yet had time, however, to fabricate and evaluate photo-cathodes made from our lower resistivity co-doped films. We (at

Hamamatsu) made 5 photo-cathodes from singly doped films (made at Northwestern). These photo-cathodes were placed in photo-tubes. Each photo-tube contains a cathode electrode, which has a GaN crystal is connected to it, and an anode electrode which faces (of course) the GaN side of the cathode. The surface of the GaN crystal was activated by cesium to reduce the work function. All of the samples were made *before* we tried co-doping, and hence the conductivity of even the best sample incorporated into photo-tubes (PTs) was a factor of about 10 worse than for our best co-doped films. The responses of these PTs was tested at Hamamatsu and are shown in Figure 4. At Rutgers University the response measurements were extended to slightly shorter wavelengths. The PTs designated SN73 and SN76 were made with films from our first trial films and had peak detective quantum efficiencies of 1-2%. In contrast, the improved films made in our second trial produced a PT with a DQE as high as 30%. As we noted above, our new films have even high conductivity and are likely to produce even better performing PTs.

Another measure of performance is what we call the figure of merit based on the sharpness of the response cutoff as determined by the ratio of the DQE at 200 nm to the DQE at 500 nm. The results for the 3 PTs for which there was a measurement at 500 nm are shown in Figure 4. As can be seen in the Figure 4, SN94 meets both performance requirements best, i.e. it has the highest DQE and the sharpest response cutoff. Although surface effects may be important, we only have electrical measurements of the films from which we can make an attempt to explain why SN94 performed the best.

Initially we had hypothesized that high carrier concentration alone would be important for better photo-cathode performance. We found, however, that this was not the case as can be seen in the top panel in Figure 5. Instead, we found that the conductivity is the key characteristic, i.e., the combination of carrier concentration and mobility must be as high as possible. This can be seen in the middle panel of Figure 5. The bottom panel of Figure 5 shows that the figure of merit also improves with increasing conductivity.

4. SUMMARY AND CONCLUSION

In summary, we have made singly and co-doped GaN films. We have demonstrated that the co-doping can be used to improve the carrier concentration and the mobility of the carriers to reduce the resistivity of the films. We have presented an explanation of why the co-doping improves the film performance. At this time we have only used singly doped films in photo-tubes, but we produced a dramatic improvement in photo-tube performance by raising the conductivity above $\sim 0.14\Omega^{-1}$ cm^{-1}. Given that with minimal sample production and testing, we have achieved $\sim 30\%$ DQE peak and about 10^{-4} DQE minimum, we conclude that it is eminently feasible to make GaN based photo-cathodes for highly efficient (> 60 % DQE) UV response while having nearly negligible ($> 10^{-6}$ DQE) below a given energy cut off. Performance enhancements are likely to come from decreasing the resistivity by optimizing the combined values of carrier concentration and mobility. Co-doping with H, O or Si, appears to be a promising technique for achieving this goal

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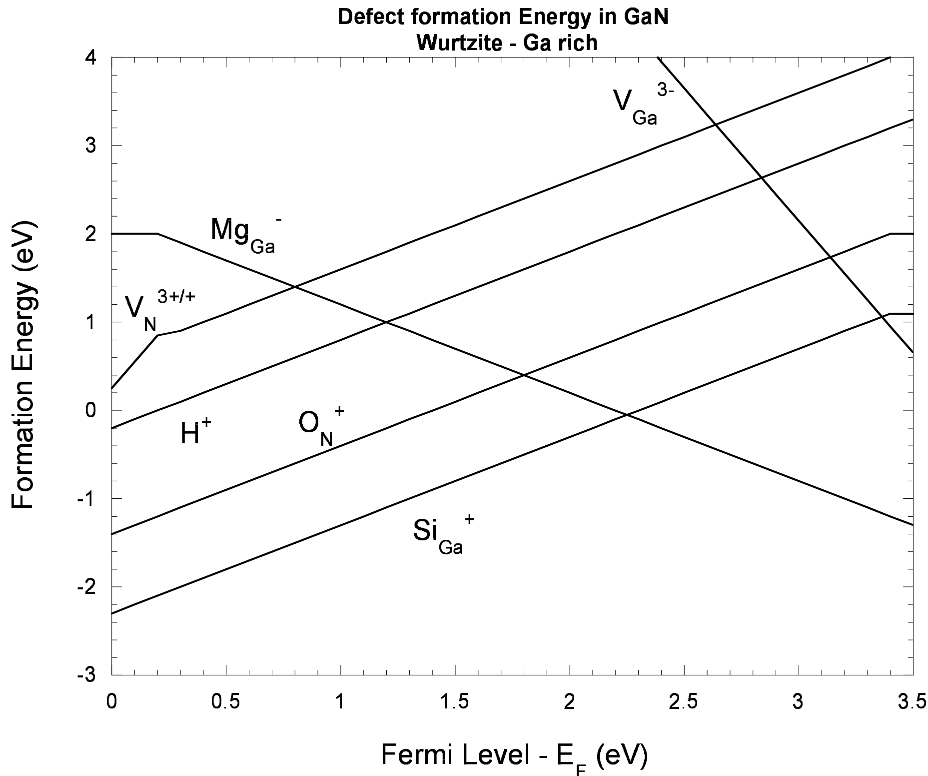

Figure 1. The energy dependence of defect formation on the Fermi level.[13,12]

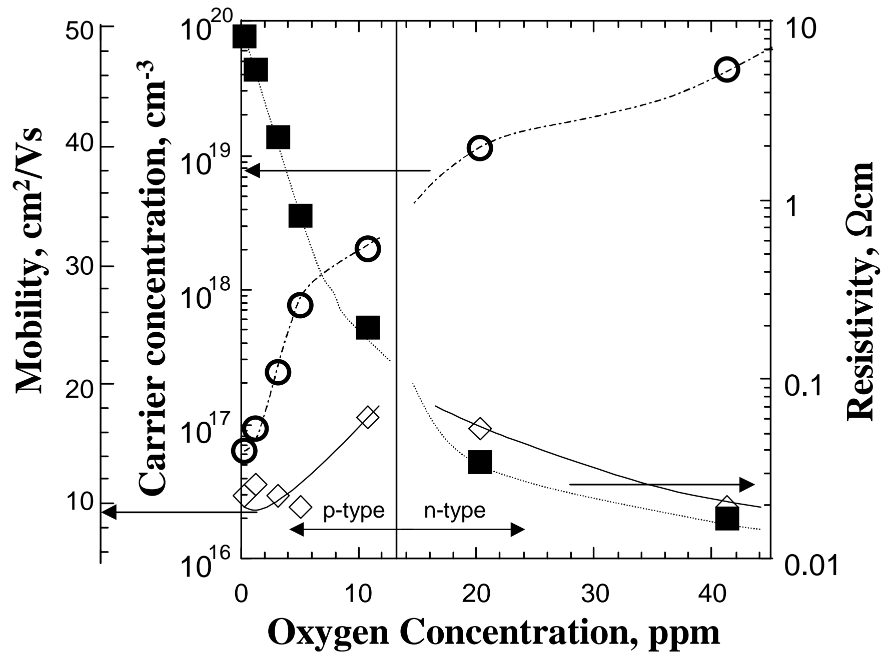

Figure 2. Mg flow rate fixed at 0.36 μmole/min and the O rate was varied. The flow rate of O is normalized to the total flow.[14]

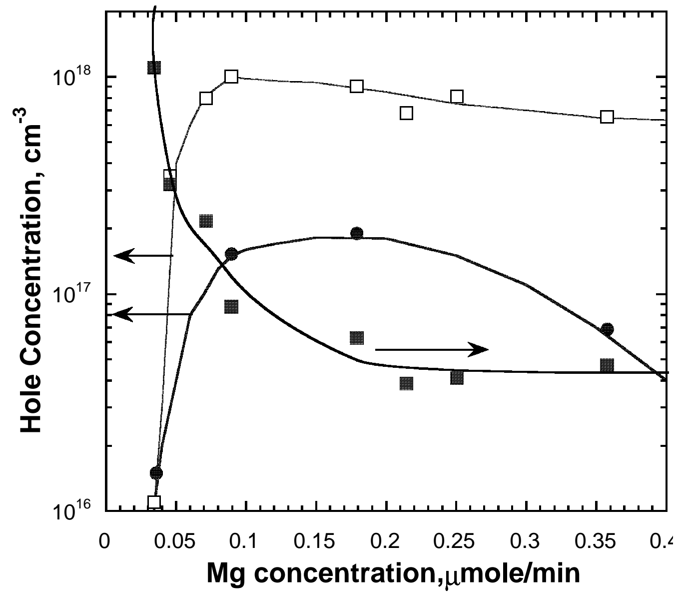

Figure 3. The O concentration is fixed at 4 ppm and the Mg flow was varied.[14]

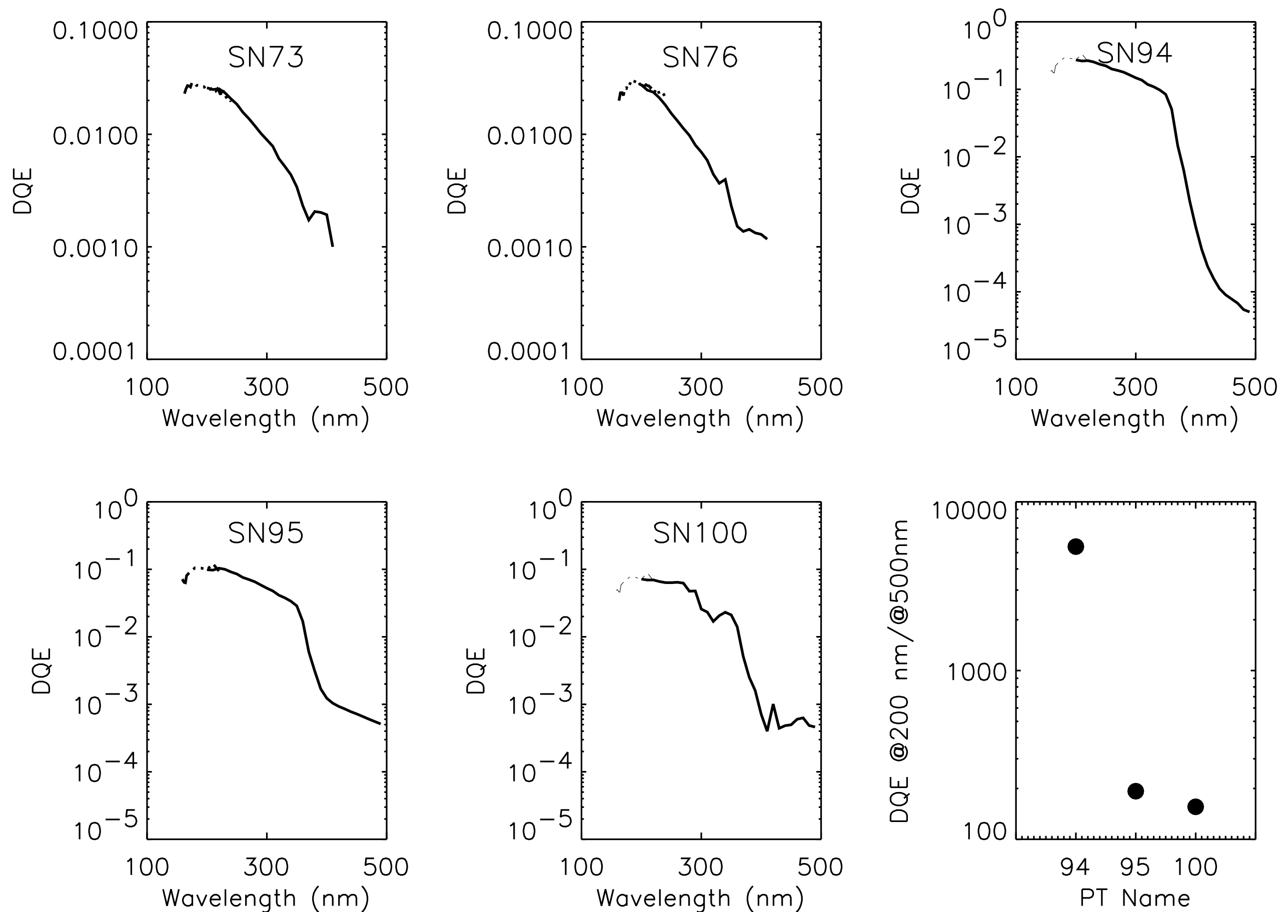

Figure 4. A summary of the response of the various PTs that were made. The SN label designates the PT label. DQE stands for detective quantum efficiency. The solid lines are from Hamamatsu; the heavy broken lines are from Rutgers; the light broken lines are the SN95 result normalized to the SN94 and SN100 data.

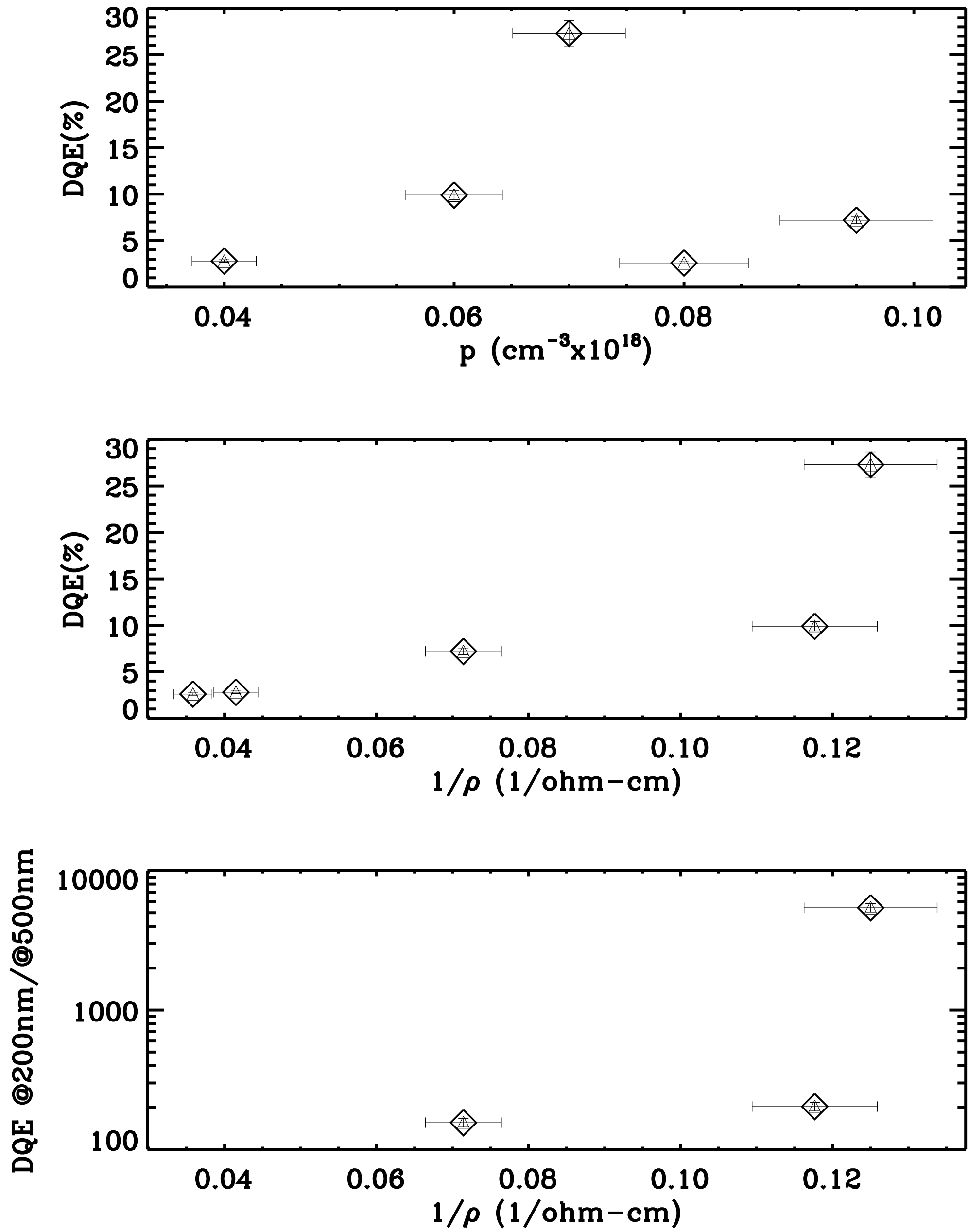

Figure 5. A comparison of the photo-cathode performance with carrier concentration (p) in the top panel and conductivity (1/resistivity) in the middle panel. DQE is the detective quantum efficiency taken from Figure 4 at 200 nm; no measurements were made at 500 nm for SN73 and SN76, hence only 3 points are shown for the figure of merit versus conductivity in the bottom panel.