Imaging hot carrier dynamics in surface nanostructures

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Introduction

The continued reduction in device dimensions requires the understanding of new phenomena such as quantum confinement, tuneable Kondo effects and Luttinger liqud states. In this respect, hot carriers and their relaxation pathways have become an intensely studied topic for the last decade. Recent work on relaxation dynamics has concentrated on the use of optical probes, such as time resolved photoluminescence[1], transient reflectivity[2], or detection of the decay products[3]. Unfortunately, optical methods do not provide direct information about hot carrier distributions as they rely on relating changes in optical properties to electron dynamics. Optical techniques also have another disadvantage in that they are mainly restricted to the study of the bulk since the penetration and escape depth of photons at optical frequencies is large. While bulk dynamics are important, coupling of electrons to surface and interface states in nanoscale systems will change the dynamics of hot carrier relaxation pathways significantly. This is particularly relevant when considering the high surface to volume ratio of low dimensional systems such as quantum dots.

Time-Resolved PhotoEmission Spectroscopy (TRPES)[4] can directly measure the electronic dynamics of hot carriers on ultrafast timescales and it has the advantage of being surface and interface sensitive. However, as this technique is spatially averaging it is not possible, for example, to investigate local variations of the electron dynamics from spatially heterogeneous systems. One method to circumvent this problem is to use a PhotoEmission Electron Microscope (PEEM) which allows surface morphology and structure to be studied with a resolution of <20nm. In this report we present data from the combination of TRPES and PEEM to study ultrafast relaxation dynamics from surface nanostructures. Two sets of experimental results are discussed. We initially present the first images of excited Ge quantum dots on Si, together with a study on the polarisation dependence of the two photon photoemission process. The second set of results discusses the temporal evolution of transiently excited carriers in the Ge quantum dots.

Experimental Setup

The output of a mode locked Ti: Sapphire laser with a pulse length less than 200fs is frequency doubled and then trebled using sum frequency mixing. The second harmonic (3.1eV, max pulse power <10KW), focused to a 100μm spot, was used for electron excitation. The angle of incidence was 69 degrees with respect to the surface normal. As the photon energy is below the photoemission threshold, a two step process involving unoccupied intermediate states is required for electron emission[5]. Thus in this configuration the PEEM image represents the lateral variation of the intermediate unoccupied states. A half wave plate was used to rotate the polarisation vector of the second harmonic beam in order to measure its affect on the 2PPE intensity. The third harmonic was also used to image via the normal photoemission process as the photons have an energy of 4.7 eV, just above the photoemission threshold for the Si(111) surface. For time-resolved measurements a fraction of the SH light was used to pump electrons into unoccupied intermediate states. The TH light was collinearly combined with the SH using a dichroic beam-splitter and used to photoemit electrons from both the normal and excited states. The probe pulse was delayed with respect to the pump pulse by a computer controlled delay stage. In this mode a series of images was taken at varying temporal delays, $\Delta\tau$, between the two beams.

The experiments were performed in a UHV-system with a base pressure of <5×10 mbar. Atomically clean reconstructed Si(111)7×7 and Si(001) 2×1 surfaces were first obtained by extensive degassing of B-doped samples (1 and 0.2 ohm cm respectively) at 600°C followed by repeated flash annealing to 1200°C for 1 min ($<2\times10^{-9}$ mbar). The surface quality was verified by observing a sharp characteristic LEED pattern for the 7×7 and 2×1 reconstructions. Ge (commercial source) was evaporated from an Omicron EFM3 at a flux of 3μA, giving an evaporation rate of 0.2ML per minute (1ML= 3.14Å) as measured by a quartz thickness monitor. The growth followed the Stranski-Krastanov mode; i.e., initial growth is in a layer-by-layer mode up to a critical thickness of 3–4 monolayers (ML) after which 3D islands nucleate to relieve the elastic strain caused by the film-substrate lattice mismatch. Images were taken of the clean Si substrate as well as of both sub and above critical layer thicknesses.

PEEM

Figure 1 shows the changes that occur in the PEEM image when Ge is progressively deposited onto a Si(001) 2×1 surface. Images were taken using just the TH of the laser. The Si(001) 2×1 surface has a workfunction of 4.85eV with the Fermi level pinned by surface states just above the valence band maximum. As the image brightness of each pixel is proportional to the photocurrent we must consider why linear photoemission can be excited by 4.7eV light from surfaces with a workfunction of 4.85eV. ARPES studies of Si(001) 2×1[6] have shown the existence of an extended metallic like state at the Fermi edge which has been attributed to disordered defects. The Si(001)2×1 surface is double domained with considerable disorder along domain boundaries Disordered defects are not easily identified in general and would not be present in our LEED measurements. We believe the presence of these defects are responsible for the linear photoemission image we see. It is worth noting that many other authors on

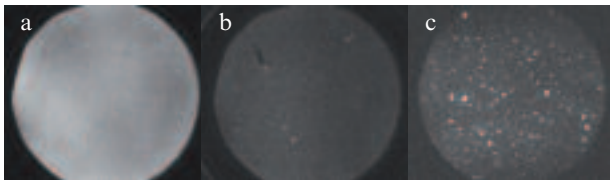

Figure 1. PEEM image of (a) clean Si(001), (b) <3ML Ge on Si(001), (c) 10ML Ge on Si(001). The field of view for each image is 50μm.

TRPES also see linear photoemission from the same surface for sub workfunction excitation which they also attribute to occupied surface states. As Ge is progressively deposited onto the surface the image becomes darker. Once the Ge layer exceeds the critical thickness, islands form to relieve elastic strain. Figure 1c shows the PEEM image for 10ML of Ge deposited on Si(001) 2×1. The image clearly shows a dramatic change between the clean Si(001) and the sub critical thickness Ge/Si(001) surfaces. Dots have formed via the Stranski Krastnow growth mode and have a size distribution ranging from 200nm to 1000nm. Why the dots appear bright compared to the background is probably due to a combination of two effects. Himerlech *et al*[7] measure the ionization potential of the strained wetting layer of the Ge/Si(001) 2×1 system and of partially relaxed islands to be 5.3 and 4.7eV respectively. This explains why in the PEEM images the initial growth of the wetting layer appears dark whilst the dots are bright. Secondly, non flat surfaces can lead to an increase in the electron density due to local field enhancements which would also tend to enhance the contrast of the dots compared to the wetting layer.

Two Photon Photoemission

Figure 2 shows the Ge/Si(111) 7×7 surface imaged using the SH output of the laser system as the photon source. At these photon energies (3.2eV) linear photoemission is not energetically possible from either the Si substrate or the Ge layer. Therefore electron emission is via two photon excitations which must involve intermediate excited states. In the case where a single non linear process is responsible for the photocurrent, the dependence of the image intensity J on the laser power P can be expressed as[5]

$$J = cP^n$$

where n is the number of photons involved in the emission process. Figure 3 shows the dependence of the local photoyield (intensity) upon the laser power. A fit of the above equation to the data gives $n \approx 2$, consistent with our assignment of 2PPE as the emission process. Images were also taken with different orientations of the incident beams polarisation vector. The area integrated intensity measured as a function of polarisation angle is shown in figure 4. As can be seen from the figure the polarisation dependence fits reasonably well with a $\cos^4(\theta)$ function indicating second order non linear effects in photoemission[5].

Time Resolved Photoemission SpectroMicroscopy

As well as imaging all electrons emitted as a result of photoabsorption, the PEEM can also give spectroscopic information by forming an image using electrons of a specific kinetic energy only. As a result a stack of images can be created which reveals the spectral electron distribution of the surface. Figure 5 shows the time

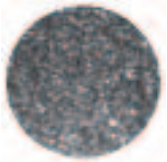

Figure 2. 2PPE image of Ge dots on Si(111) taken using the SH of the laser as the photon source. The field of view is 20μm.

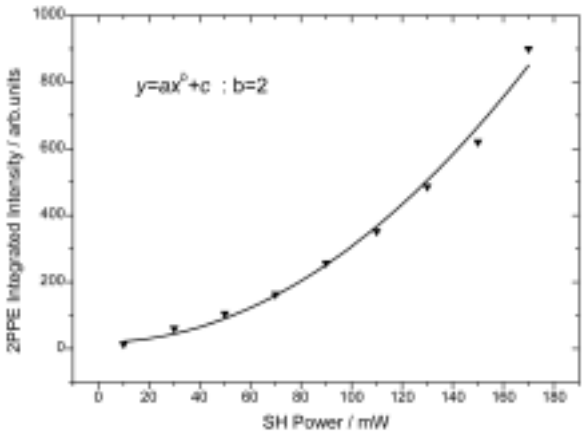

Figure 3. Image intensity as a function of laser power for the Ge/Si(111) surface containing Ge dots.

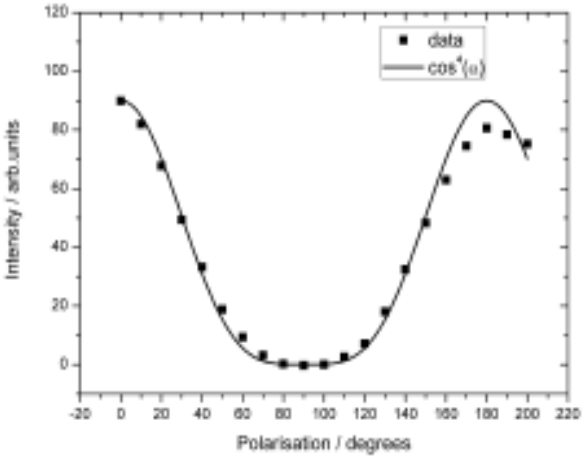

Figure 4. Dependence of the local photoemission intensity on the orientation of the electric field vector. s-polarisation occurs at θ=90°.

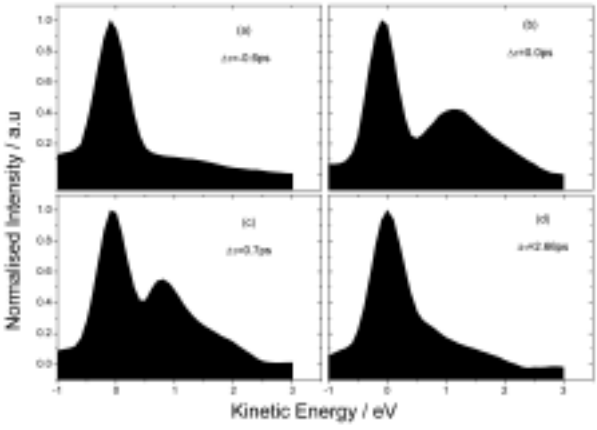

Figure 5. Time resolved photoelectron spectrum from a Ge/Si(111) surface containing Ge dots. The time delay between the pump and the probe beams are indicated in the figure.

resolved spectrum from a Ge/Si(111) 7×7 surface containing Ge dots. The spectrum was produced by spatially integrating the photoyield for a series of kinetic energy images. The spectrum at $\Delta\tau$=–0.6ps consists mainly of the linear photoemission peak. This peak is presumably the tail of the S1 surface state of Si(111) or a surface state

of Ge(111) which are metallic like and have a non zero DOS at the fermi level. The intensity of this peak falls for negative KE due to the cutoff of the energy analyser. At $\Delta\tau$ =0.0ps, at which the probe beam is in temporal overlap with the pump beam, there is an increase in the photoyield at kinetic energies ranging from 0.5 to 3 eV. This corresponds to unoccupied surface and conduction band states being transiently populated by the pump beam. Initially a population of electrons is excited by the pump pulse into a narrow band of conduction states at $\Delta\tau = 0$. Thermalisation, achieved through e-e scattering which randomizes both the energy and the momentum of the electrons, rapidly produces an equilibrium non-degenerate distribution which can be described by Maxwell-Boltzmann statistics. As can be seen from Fig.5b, the excited state peak clearly has the form of a Boltzmann distribution which indicates that thermalisation of the hot electron gas must occur on time scales faster than 200fs, the temporal resolution of the experiment. In order for the excited electron gas to lose energy (and to relax momentum) electrons must scatter from phonons of the system. In this manner, excess electronic energy is converted to heat in the lattice. In homopolar semiconductors such as Ge and Si, this process occurs by deformation potential scattering. At $\Delta\tau > 0.0$ps the excited state peak starts to narrow and shifts to lower kinetic energies consistent with both cooling of a hot electron distribution and relaxation of conduction band electrons into gap surface states toward the valence band by phonon emission. For $\Delta\tau > 4$ ps the excited state disappears completely.

Conclusion

In summary we have shown that using the technique of time resolved spectromicroscopy, hot electron dynamics of surface nanostructures can be studied. In particular we show that this technique is well suited for studying excited state dynamics in systems which have an indirect bandgap. Implementation of a higher energy probe, obtained by using the fourth harmonic of the Ti:Sapphire system, will enable occupied surface states to also be measured which will provide an absolute energy reference.

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